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# Laboratory Evaluation of High-Temperature Destruction of Polychlorinated Biphenyls and Related Compounds

Dayton Univ, Ohio Research Inst

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A specialized laboratory technique incorporating a two-stage quartz system was utilized for determining the thermal destruction properties of PCB's and related compounds. With this system, a small sample was first converted to the gas phase, then exposed to high-temperature destruction conditions. Critical parameters of temperature and residence time were accurately measured. When PCB's were exposed for one second to a series of high-temperature air environments, it was found that initial decomposition occurred at approximately 640°C; greater than 95% molecular destruction was obtained at 740°C; and 99.995% molecular destruction was found at 1000°C. Also, it was determined that PCB's (and certain related compounds) thermally decompose to low molecular weight products, as yet unidentified.

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# LABORATORY EVALUATION OF HIGH-TEMPERATURE DESTRUCTION OF POLYCHLORINATED BIPHENYLS AND RELATED COMPOUNDS

by

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## FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

Surplus, unwanted, and highly hazardous industrial chemicals pose safety hazards to the public and are potential sources of environmental contamination. The study reported herein presents thermal decomposition data for several organic chemicals based on a specially designed laboratory technique.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

## ABSTRACT

Polychlorinated biphenyls (PCB's) are extremely stable synthesized compounds which have reached global distribution in the environment. These compounds have been found to be particularly dangerous to certain species and ecosystems. Accordingly, further production of PCB's in the United States will cease by October 31, 1977, and existing stocks of these hazardous materials will eventually be destroyed. However, as there is considerable disparity as to what constitutes acceptable thermal disposal criteria for PCB's, this study was undertaken to provide basic data on the thermal destruction of these compounds.

A specialized laboratory technique incorporating a two-stage quartz system was utilized for determining the thermal destruction properties of PCB's and related compounds. With this system, a small sample was first converted to the gas phase, then exposed to high-temperature destruction conditions. Critical parameters of temperature and residence time were accurately measured. When PCB's were exposed for one second to a series of high-temperature air environments, it was found that initial decomposition occurred at approximately 640°C; greater than 95% molecular destruction was obtained at 740°C; and 99.995% molecular destruction was found at 1000°C. Also, it was determined that PCB's (and certain related compounds) thermally decompose to low molecular weight products, as yet unidentified.



This report was submitted in fulfillment of Grant No. R803540-01-0 by the University of Dayton Research Institute under the sponsorship of the U.S. Environmental Protection Agency. This work was done during the period August 15, 1976 through January 15, 1977.

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# SECTION I

# BACKGROUND

The original objective of this research project was to determine, for a number of selected pesticides, the temperature at which molecular destruction was effectively completed at a residence time of <2 seconds. In order to achieve this objective, it was first necessary to develop the laboratory apparatus and techniques capable of providing such data.

## PYROLYSIS GAS CHROMATOGRAPHIC APPROACH

The laboratory facility for acquiring thermal destruction data centered about a pyrolysis gas chromatography setup utilizing a Chemical Data Systems Pyroprobe 100 and a Varian 2400 gas chromatograph. The basic approach was to deposit a microgram size sample of a pesticide upon a uniform, platinum ribbon. The ribbon was then placed in a chamber immediately upstream of a gas chromatographic column assembly. After admitting air into the chamber, the platinum ribbon and pesticide sample were subjected to a defined thermal pulse. The thermal decomposition products were then swept with an inert carrier gas (helium) into the chromatographic instrument and analyzed.

A considerable amount of time and effort was spent in developing the pyrolysis gas chromatographic apparatus. A unique feature of this technique was that both the temperature of the platinum ribbon and the time duration at that temperature could be very accurately measured. In order to obtain these data, a special electronic circuit was assembled. This circuit simultaneously sensed the voltage (E) across the ribbon, along with the current (I) through it, and thereby generated an output proportional to E/I. This output represented the average resistance of the platinum ribbon during a timed interval, thereby providing a direct measurement of the ribbon temperature.

The approach of using a pyrolysis gas chromatographic technique, however, was not successful. While preliminary work had indicated that the technique was promising for samples of low volatility, more detailed work showed otherwise. In short, it was found that the thermal degradation of a pesticide at elevated temperatures on the platinum ribbon produced variable and inconsistent results. The basic problem was that the pesticide

vaporized (at least partially) before it reached degradation temperatures -- even at the extremely rapid temperature rise of 50°C per millisecond.

## TWO-STAGE QUARTZ TUBE SYSTEM

At this point in the research project, the pyrolysis gas chromatography approach was suspended, and research efforts turned to a two-stage quartz tube system. In this system, the sample was vaporized in a low-temperature chamber, and then carried in a stream of flowing air into a high-temperature destruction zone. This system was successfully developed, and is described in detail later in this report.

Coincidental with our developing a workable system to evaluate the thermal destruction properties of organic hazardous wastes, the Kepone problem emerged. The serious environmental problems concerning Kepone manufacturing operations in Hopewell, Virginia, have been widely publicized. Large-scale disposal and environmental cleanup problems were associated with Kepone found in soil, water, sewage sludge, etc. Shortly after the severity of this contamination problem became apparent, a Kepone Task Force was formed within the Environmental Protection Agency (EPA). As task force discussions progressed, it was concluded that high-temperature controlled incineration offered the best potential for successful disposal of this hazardous pesticide. However, thermal degradation data for Kepone were not available, and would have to be generated.

For this reason, the project officer requested that the University of Dayton alter its schedule of work under Grant No. R803540-01-0 in order to conduct a study of the thermal destruction properties of Kepone. The motivation for this work was a request from EPA ORD KEPONE TASK FORCE pointing out the need for thermal degradation data to assist cleanup operations of the hazardous environmental situation caused by Kepone pollution in Hopewell, Virginia. Accordingly, the study was designed to provide data from which to establish requirements for the thermal disposal of Kepone. The specific objective of the laboratory effort was to identify destruction temperature characteristics of the vaporized pesticides at preselected residence times. A major part of the program involved examination of the gas phase destruction behavior of the selected pesticides for completeness of destruction and identification of decomposition products while in a controlled-flow, high-temperature air environment. (Note that this system differs from a pyrolysis, or oxygen deficient technique.)

The findings of this laboratory study clearly pointed out that the complicated chemical nature of pesticide thermal destruction products is strongly dependent on the temperature and residence time that the pesticide encounters. Therefore, it is

most important to acquire precise analytical data which identify and quantify decomposition products relative to exposure temperature and residence time. The laboratory approach is ideally suited for obtaining these basic data, which are needed to insure logical decision making in planning the thermal disposal of pesticides.

The Kepone work was handled as a high-intensity, short-turnaround project. For comparison purposes, the chlorinated pesticides Mirex and DDT were also studied at the same time. By Spring of 1976, substantial data had been developed and a special technical report covering the work on all three pesticides had been submitted to the EPA Project officer for distribution to involved parties. This report, EPA Report 600/2-76-299 "Laboratory Evaluation of High Temperature Destruction of Kepone and Related Pesticides," has formed the data base in support of pilot plant incineration studies of Kepone and Kepone contaminated sludge.

## POLYCHLORINATED BIPHENYLS (PCB's)

Following the completion of the Kepone work, a program was initiated, at the request of the EPA Project officer, to similarly study the thermal decomposition properties of polychlorinated biphenyls. The need for this work is well justified by the serious disposal problems related to the widespread environmental contamination of PCB's. At the present time, some 750 million pounds of PCB's are in use within the United States, with another 750 million pounds already having entered the environment.

Over the past several years, increased attention has been focused on PCB's as it has been established that they persist and accumulate in the environment. PCB's, even at low part-per-million levels, cause adverse effects in fish and other aquatic life. Also, laboratory tests have shown PCB's to cause gastric disorders, skin lesions, reproductive failures, and tumors in mammals. For these reasons, the EPA now considers PCB's to be a significant hazard to human health as well as to the environment.

The remainder of this report is concerned with the PCB thermal destruction studies carried out at the University of Dayton Research Institute.

## SECTION II

## INTRODUCTION

Polychlorinated biphenyls (PCB's) were introduced commercially in 1929. They were initially utilized as dielectric fluids in transformers and capacitors; however, since that time PCB's have found a multitude of applications. Further, it was not until 1966 that PCB's were identified as widely distributed environmental contaminants [1].

PCB mixtures have unusual and almost unique properties. They are clear liquids possessing both thermal stability and resistance to biological degradation. Also, as a class of chemical compounds, PCB's are non-flammable, and have low vapor pressure, low water solubility, high solubility in most organic compounds, and high dielectric constants. As a result of their unusual material properties, PCB's have been used over the past 40 years for many applications other than as dielectric fluids. PCB's have been formulated into varnishes, waxes, synthetic resins, epoxy and marine paints, sealants, printing inks, textile coatings, glues, cutting oils, carbonless reproducing paper, and protective coatings for wood, metal, and concretes. PCB's have also been used as plasticizers, solvents for adhesives, hydraulic fluids, flame retardants, heat exchanger fluids, petroleum additives, and pesticide extenders.

Initially, PCB's were not considered to be very toxic. Indeed, they demonstrated a rather low acute toxicity in animal studies [2]. However, they have since been shown to be potent chronic toxicants [3]. PCB's readily undergo biomagnification by successive members in a food chain, e.g., plankton to fry to fish to birds, etc. Also, because of their resistance to biodegradation, PCB's persist for long periods of time in water and biota. Related research has shown that water containing even very low levels of PCB's (<10 ppb) inhibits the growth of shrimp, oysters, and plankton [4,5]. Also, when PCB's are ingested in animals and humans, they are preferentially stored in the body's fatty tissues. This is a serious matter as recent studies [6-8] have linked PCB exposure to liver and pancreatic cancer, along with melanoma skin cancer. For a thorough understanding of the wide ranging problems associated with the global distribution of PCB's in the environment, the reader is referred to the research works of Risebrough et al. [9], Gustafson [10], Jensen

[11], Fishbein [12], Selikoff [13], Carnes et al. [14], Ruopp et al. [15], and others [16-19].

Production of PCB's in the United States will cease by October 31, 1977 [20]. Also, measures are underway to restrict the importing of PCB's and products containing PCB's. Meanwhile, the research continues for acceptable substitutes for PCB's within the electrical industries [21]. In view of the persistency, chronic toxicity, and structural stability of various PCB molecules, adequate disposal of these unwanted materials represents a challenging task. As the most likely method of permanent disposal is through the use of specialized high-temperature incineration, the University of Dayton Research Institute (UDRI) was requested by the EPA Project Officer to provide some basic thermal destruction data on PCB's. Accordingly, a laboratory investigation was undertaken to determine the high-temperature destruction properties of PCB's.

The specific objectives of this investigation were:

(1) to determine the degree of molecular thermal destruction as a function of exposure temperature;

(2) to determine the effects of residence time at high-temperature; and

(3) to determine whether other toxic decomposition products might be produced as a result of the high-temperature exposure.

## SECTION III

## CONCLUSIONS

1. PCB's are more thermally stable than Mirex -- a very thermally stable pesticide.

2. Commercial PCB's undergo decomposition in air between 640 and 740°C at a residence time of ~1 second. PCB's subjected to a very high temperature exposure (1000°C for 1 second in air) yield a destruction percentage of 99.995.

3. Residence time is a strong factor in the high-temperature destruction of PCB's.

4. Upon thermal stressing in air, PCB's decompose to low-molecular weight products. (These products were not identified in this study.)

5. For a given thermal exposure, the lower molecular weight PCB's are less thermally stable than the higher molecular weight PCB's.

6. Compounds related to PCB's--biphenyl, dibenzofuran, dibenzo-p-dioxin, and hexachlorobenzene--demonstrate thermal destruction properties comparable to PCB mixtures.

## SECTION IV

## RECOMMENDATIONS

This study has experimentally measured the destruction temperature - residence time relationships for various PCB compounds and mixtures of PCB's. To further clarify the thermal destruction properties of these particular compounds, the following actions are recommended:

1. Determine the thermal destruction and effects of residence time at temperatures greater than 1000°C.

2. Make complete analyses of degradation products and effluents. (Further research is required to design and develop a laboratory system capable of providing this information.)

3. Investigate the thermal destruction behavior in moist air.

4. Study the flame mode of decomposition and compare results to the non-flame mode of destruction.

5. Eventually test the scale-up validity of PCB thermal decomposition.

## SECTION V

## STABILITY OF PCB's

The stability of various PCB compounds in the environment has been the subject of numerous investigations. At the present time, it is generally agreed that PCB compounds will persist in the ecosystem for a long period of time. However, certain mechanisms of degradation have been identified [22-25]. Various PCB compounds can be dechlorinated by ultraviolet light, while others are vulnerable to microbial attack. It has generally been observed that the lower molecular weight PCB's are more readily biodegraded, while the heavier compounds exhibited greater overall stability.

PCB's can withstand long-term heating (200-300°C) in air without decomposing. This high thermal stability has led to wide industrial applications; however, this same property also helps account for widespread occurrence of PCB's in the ecosystem. For example, it is well known that many PCB's have entered the environment through inadequate incineration and indiscriminate burning of wastes. At the present time, most of the conventional incineration processes do not produce sufficient exposure temperature or residence time to break down these stable compounds. Consequently, the PCB's have been merely vaporized, and thus further dispersed.

In the available literature pertaining to the thermal disposal of PCB's, considerable disparity is found in the prescribed conditions for thermal disposal. In addition, since this thermal disposal information was gathered using a variety of incineration equipment and methods, there are many variables which complicate interpretation. To illustrate the broad range of specified incineration conditions, two extreme examples are presented. PCB's contained in wet sludges were reported to have been destroyed in an after-burner when exposed to 593°C for a period of 0.1 second [26]. At the other extreme, it is contended [27] that PCB's should be exposed to 1316°C for a time duration of 2.5 seconds. There are many other specified conditions in the literature [28-31] which fall between these extremes.

In view of the widely differing accounts of PCB thermal stability, a thorough laboratory investigation was undertaken. This study was designed to determine the high temperature decomposition properties of the various PCB's and related compounds.

The information obtained from these experiments will be of vital assistance in developing future pilot scale thermal decomposition tests.

## SECTION VI

## RATIONALE OF LABORATORY APPROACH

In order to determine the high-temperature destruction characteristics of an organic molecule, it is necessary to obtain precise information on certain crucial parameters. It is important that the system temperature be accurately determined, along with the residence time, i.e., the time interval during which the molecule experiences the destructive temperature. Another critical parameter that must be fulfilled in such an evaluation is that there be an adequate supply of air so that the destruction takes place in an oxidative environment, as opposed to an atmosphere containing insufficient oxygen. Lastly, an important factor is the composition of the high-temperature environment, e.g., water content, presence of other gases, and interfering solid materials.

The laboratory approach to establishing a material's high temperature, non-flame destruction characteristics has certain distinct advantages. First, one can examine the undiluted sample; therefore, no interferences are encountered from other materials. Second, the composition of the high-temperature environment can be precisely established by using compressed air of known quality and employing in-line filters to remove water, oil, and other foreign materials. Next, by using a technique whereby a small sample is gradually vaporized and then passed through a high-temperature zone, an excess of oxygen is assured, thus avoiding the possibility of a pyrolytic reaction occurring. Further, it is possible to evaluate the behavior of the pure sample on the molecular level. By vaporizing the sample prior to its exposure to the high-temperature environment, one can be assured, based on the kinetic theory of gases [32], that the molecules do indeed experience the actual average temperature. Finally, the laboratory evaluation of a sample's destruction characteristics can be accomplished quickly and economically with minimum environmental risk.

It is important to note that during incineration of waste materials, a certain amount of energy must be applied just to change the organic compounds from their usual state (whether it be solid or liquid) to the gas phase. These phase transitions, apart from requiring additional energy, also require an undefined amount of exposure time to the high-temperature source. There-

fore, it is almost certain that in the case of waste materials containing PCB's, some molecules do not encounter the prescribed incineration temperature. In short, even though the temperature within a chamber is known, it does not necessarily mean that all substances within that chamber have indeed attained thermal equilibrium. However, if all of the substances in the chamber are in the gas phase, one can safely assume that the individual molecules have (with sufficient time exposure) achieved the average temperature of that environment.

For similar reasons, the laboratory evaluation of a sample's residence time is considerably simplified over that of measuring residence time in a large scale unit. When a gas is passed through a long narrow-bore flow path (in the laminar flow region), radial dispersion can be neglected and the main factor affecting the residence time distribution is longitudinal diffusion. However, for flow paths that are of large diameter, mixing chamber, or multichamber configuration, radial dispersion is the major factor affecting the variation in residence time of the transported molecule [33]. Figure 1 depicts the residence time relationships for gas phase compounds passing through the two different flow paths. The exact contours of these generalized profiles are dependent upon the nature of the flow, i.e., laminar or turbulent, and other factors such as wall composition [34] and surface finish. However, in general, residence time can be accurately measured with a narrow-bore flow path, whereas for the large diameter flow path, molecular residence time can, at best, only be approximated. This situation can be illustrated by observing in Figure 1a that some molecules can pass through the large diameter flow path in a very short time; while some molecules, as evidenced by the asymptotic behavior of the right-hand side of the same curve, can remain in the high-temperature region for an extended period of time.

The approach for obtaining high-temperature destruction data on the PCB's utilized a discontinuous system where the thermal stressing of the sample and product analysis are performed separately. Using this approach, various PCB samples and related compounds were evaluated in a series of tests where the sample was first vaporized and then transported through a narrow-bore, high-temperature zone by a controlled flow of air. In this way, average temperature and residence time were firmly established. These tests were conducted at a series of temperatures ranging from $\sim$300°C to 1000°C. Also, the effluent from each high-temperature test was passed through a trapping medium and the collected fraction was subsequently analyzed by gas chromatography.

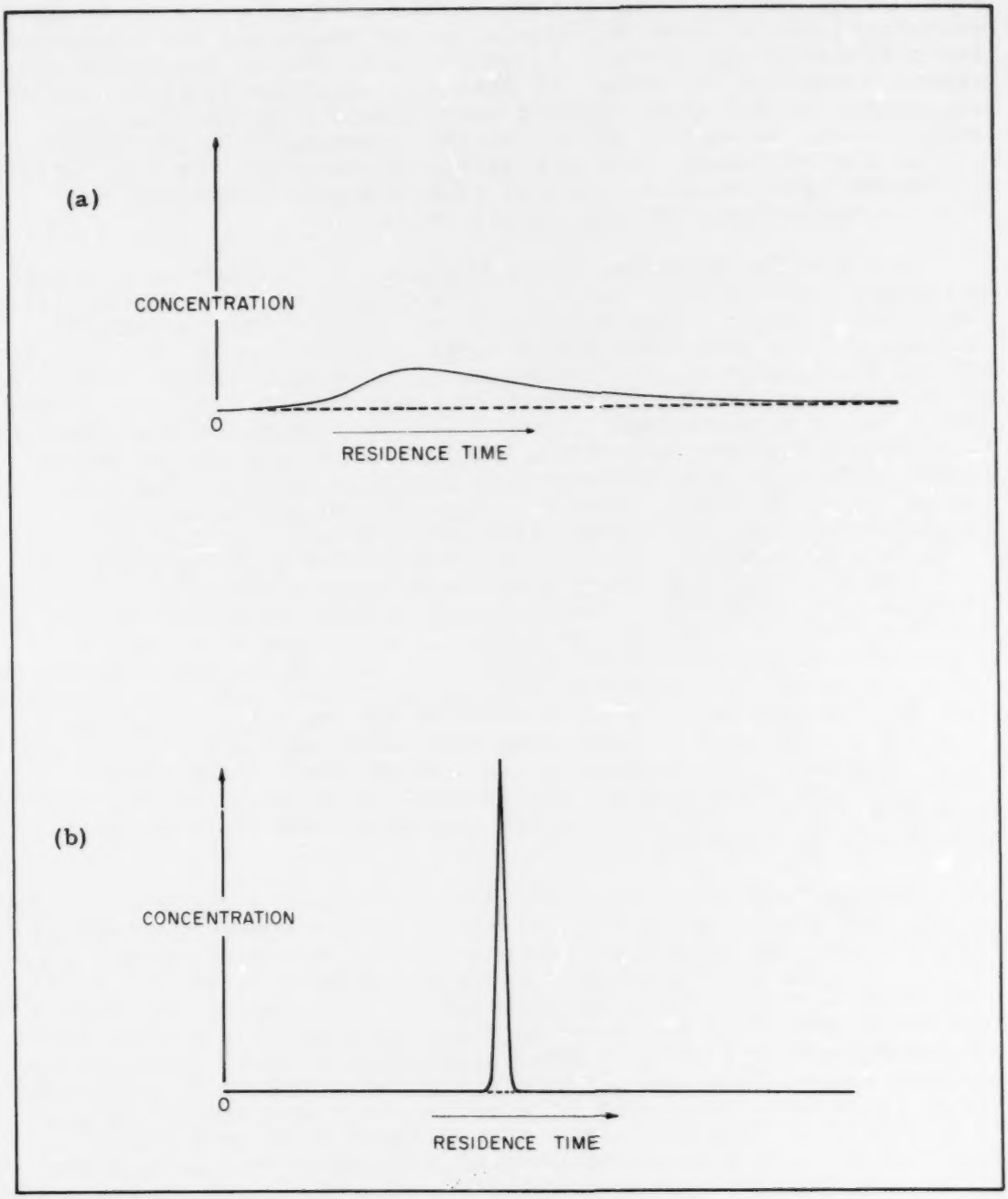



Figure 1. Residence time of gas phase molecules. (a) Large diameter, mixing chamber, or multichamber flow path. (b) Narrow-bore flow path.

## SECTION VII

## EXPERIMENTAL PROCEDURES

### SELECTION OF SAMPLES

The primary objective of this study was to obtain basic experimental data pertaining to the thermal destruction properties of PCB's. To accomplish this objective, we examined commercial PCB mixtures and pure samples of those PCB isomers that have received previous study [35] and are widely dispersed in the environment [36]. Accordingly, the isomers selected for study were 2,5, 2',5,' -tetrachlorobiphenyl and 2,5,2',4',5'-pentachlorobiphenyl. Also, to better understand the PCB thermal destruction process, other compounds were included in this study. Biphenyl was included as it is the skeleton member of the PCB family. Although decachlorobiphenyl is not present in significant quantities in the various commercial PCB mixtures, the thermal destruction behavior of this compound was considered of vital importance. It was anticipated that this compound would represent the "worst case" with respect to thermal exposure needed for destruction. Another chlorocarbon, hexachlorobenzene, was included in this study for comparison purposes. It was known from previous work that hexachlorobenzene possesses very high thermal stability.

In the past, commercial mixtures of PCB's that were manufactured in Europe were found to contain small concentrations of highly toxic chlorinated dibenofuran compounds [37]. Also, low levels of chlorinated dibenzofurans were found to occur when water solutions of certain PCB's were subjected to photolysis [38]. Therefore a sample of the relatively low-toxicity dibenzofuran was included for examination of thermal destruction. This non-chlorinated compound could be easily examined with the present laboratory system. In addition, it was hypothesized that the thermal destruction properties of chlorinated and non-chlorinated dibenzofuran would be closely related. (This hypothesis will be subjected to thorough testing in the near future.) For similar reasons, and in view of the recent interest in the chlorinated dibenzo-p-dioxins [39-41], it was also decided to obtain thermal destruction data on dibenzo-p-dioxin, a non-chlorinated compound.

The specific compounds examined in this study are listed and described in Figure 2. The biphenyl, hexachlorobenzene, di-

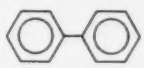
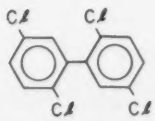
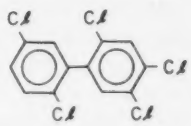
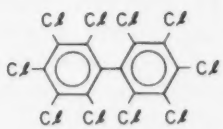
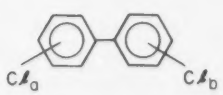
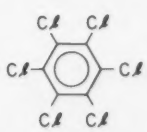
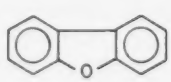
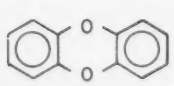
| COMPOUND | STRUCTURE | EMPIRICAL FORMULA |
|---|---|---|
| Biphenyl |  | $C_{12}H_{10}$ |
| 2, 5, 2', 5', - Tetrachlorobiphenyl |  | $C_{12}H_6Cl_4$ |
| 2, 5, 2', 4', 5', - Pentachlorobiphenyl |  | $C_{12}H_5Cl_5$ |
| Decachlorobiphenyl |  | $C_{12}Cl_{10}$ |
| Polychlorinated Biphenyls |  | $C_{12}H_{10-(a+b)}Cl_{a+b}$ |
| Hexachlorobenzene |  | $C_6Cl_6$ |
| Dibenzofuran |  | $C_{12}H_8O$ |
| Dibenzo-p-dioxin |  | $C_{12}H_8O_2$ |

Figure 2. Description of chemical compounds.

benzofuran, dibenzo-p-dioxin, and pure PCB isomers were obtained from Analabs, Inc., North Haven, Connecticut. The seven PCB mixtures used in this study were Aroclor numbers 1221, 1232, 1242, 1248, 1254, 1260, and 1262, respectively. This series of Aroclor samples was obtained from the National Environmental Research Center, Research Triangle Park, North Carolina.

## THERMAL DESTRUCTION TESTING

The temperature necessary to vaporize a PCB mixture was determined by conducting a thermogravimetric analysis with the heaviest of the selected PCB mixtures, specifically Aroclor #1262. This analysis was conducted using a Fisher Series 100 thermogravimetric instrument with a flow of 60 ml/min of dried air passing through the sample region. The temperature was then programmed from ambient to 915°C at the rate of 10°C per minute. A thermogravimetric tracing for Aroclor #1262 is shown in Figure 3.

Following this thermogravimetric work, quantities of each of the selected pure compounds and commercial PCB mixtures were weighed and dissolved in a suitable volatile solvent (90% n-hexane + 10% acetone). Each sample was then subjected to a series of preliminary thermal destruction tests while in flowing dry air. These preliminary tests used the same instrumentation and procedure as a previous study involving the high-temperature destruction of the pesticides Kepone, Mirex, and DDT [42]. The description of the instrumentation and associated procedures are presented in Appendix I.

The results of the preliminary testing clearly revealed that the entire series of samples (those described in Figure 2) possessed considerable thermal stability. Furthermore, these preliminary tests showed only small differences between the thermal destruction behavior of the least stable and the most stable of these compounds.

In view of the similar thermal destruction behavior of these compounds, we combined the pure compounds and examined them in the high-temperature apparatus as a highly diluted mixture in flowing air. By employing this combined sample technique, slight differences in thermal destruction behavior were readily measured. The data scatter associated with the subtle variations in thermal exposure, as observed in the previous individual tests, was eliminated. With this combined sample technique, each species experienced an identical thermal exposure.

This combined sample technique required a slightly different sample vaporization procedure. A process of step-wise programmed heating over a 10 minute interval was used to slowly vaporize the combined sample in order of volatility. By using this procedure, a highly diluted, multicomponent sample was

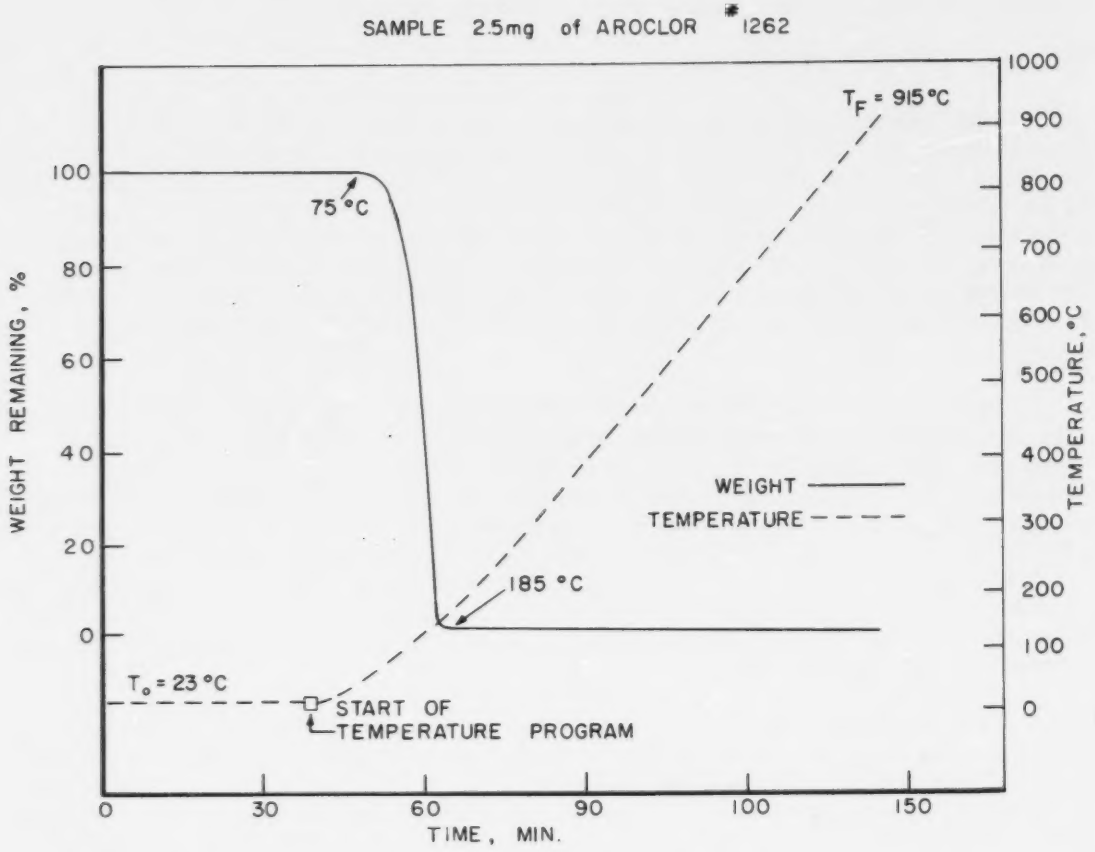



Figure 3. Thermogravimetric analysis of Aroclor #1262.

passed through the high-temperature destruction region of the quartz tube. This gradual vaporization procedure produces a high dilution of organic compounds in the flowing air, thereby minimizing the high-temperature interaction of sample and decomposition products. The entire group of samples was examined for high-temperature destruction behavior using this procedure.

## RESIDENCE TIME CONSIDERATIONS

The average high-temperature exposure of a sample molecule can be measured using the quartz-tube apparatus described in Appendix I. Also, accurate measurements of mean residence time can be obtained (see Appendix II) if accurate data are available on the outlet gas volume flow, the average exposure temperature, and the differential pressure for the quartz tube system.

Even though the mean residence time can be accurately determined, additional information is needed concerning the distribution of the residence times of different molecules. The residence time distribution of molecules can be studied in the same manner as if they entered the quartz tube as a concentrated narrow pulse (Appendix III). Also, the behavior of different molecular weight substances at different temperatures has been investigated. It was found that different molecular weights produced only a very small effect on the respective residence time distribution; however, the residence time distribution was strongly dependent upon temperature, as described in Appendix III. Even so, a fairly small tolerance can be applied to the mean residence time and still envelop the rapidly migrating molecules.

## SECTION VIII

## RESULTS AND DISCUSSIONS

From the results of the preliminary high-temperature destruction tests, it was determined that almost no thermal breakdown occurred at temperatures below 550°C. Therefore, the second series of tests using the slow evaporation of combined sample compounds was started at ∿550°C. It was also learned from the earlier tests that intense thermal decomposition occurred in this region.

### DETERMINATION OF THERMAL DESTRUCTION PROFILES

A series of tests was designed to cover the approximate range of 550°C to 800°C. These tests were conducted using a total of 40 micrograms of combined sample and a sample vaporization of 10 minutes for each test. By controlling the air flow through the folded quartz tube, mean residence time in the high-temperature zone was maintained at 1.0 ± 0.1 seconds. The trapped effluent products were then subjected to the programmed temperature gas chromatographic analysis as described by the instrumental conditions listed in Figure 4.

The results of these analyses are presented in Table I, where it is seen that the actual temperature range covered by this series of experiments starts at 562°C and extends to 801°C. The data obtained from this series of tests on combined samples were plotted on a single graph as shown in Figure 5 (note that weight percent remaining is displayed logarithmically). The same data were also plotted on two other graphs (Figures 6 and 7) having an expanded temperature axis; however, the thermal destruction profile for each compound was plotted using its respective data points.

From Figure 6, it is interesting to observe that decachlorobiphenyl and hexachlorobenzene have approximately the same thermal stability. Also, from the same figure, it is seen that biphenyl, dibenzofuran, and dibenzo-p-dioxin have somewhat similar thermal stabilities. Figure 7 shows the two extremes of the PCB family, namely the non-chlorinated biphenyl and the chlorine saturated decachlorobiphenyl. It is probable that the two compounds represent the thermal stability boundaries of the PCB family. Indeed, Figure 6 indicates that the tetrachloro-

GAS CHROMATOGRAPHIC CONDITIONS

| | |
|---|---|
| Instrument | Tracor 550 |
| Analyst | W. Rubey |
| Date | October 15, 1976 |
| Column: | |
| tubing material | Pyrex |
| tubing length | 1.8 meters |
| tubing bore | 3.5 mm |
| Stationary Phase | OV-1 Silicone |
| weight | 3% |
| Support | Chromosorb-W, HP Grade |
| mesh | 100/120 |
| Carrier Gas | Helium |
| inlet pres | 1.8 abs atmo |
| linear velocity | 10 cm/sec |
| outlet flow | 16 ml/min |
| Chart Advance | 0.5 cm/min |
| Read Out | 1.0 mv full scale |
| Sample | PCB Compounds |
| size | 40 µg total |
| Detector | HFID |
| range | $10^{-9}$AFS |
| attenuation | see chromatograms |
| Gas Flows, ml/min | |
| hydrogen | 50 |
| air | 350 |
| split ratio | none |
| Temperatures, °C | |
| detector | 320 |
| injector | RT |
| column: | |
| initial | 40 |
| final | 270 |
| program rate | 14 °C/min |
| Sample Solvent | n-Hexane |
| concentration | 5 µg/µl |

Figure 4. Programmed temperature GC analysis conditions.

## TABLE I. WEIGHT PERCENT REMAINING AFTER ONE SECOND EXPOSURE* TO RESPECTIVE TEMPERATURES

| Compound | $\bar{T}_2$, Exposure Temperature (°C) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 562 | 590 | 629 | 679 | 694 | 708 | 722 | 742 | 801 |
| Biphenyl | 100 | 100 | 78.1 | 28.8 | 5.0 | 0.36 | 0.08 | --- | --- |
| Dibenzofuran | 100 | 100 | 86.4 | 48.2 | 14.5 | 1.16 | 0.23 | --- | --- |
| Dibenzo-p-dioxin | 100 | 98.6 | 80.8 | 31.5 | 6.8 | 0.34 | --- | --- | --- |
| Hexachlorobenzene | 100 | 100 | 94.4 | 77.8 | 55.6 | 33.3 | 13.9 | 4.2 | < 0.1 |
| Tetrachlorobiphenyl (2, 5, 2', 5') | 100 | 97.2 | 83.3 | 55.6 | 33.3 | 9.0 | 0.69 | --- | --- |
| Pentachlorobiphenyl (2, 5, 2', 4', 5') | 100 | 96.9 | 87.5 | 57.8 | 39.1 | 13.7 | 1.12 | --- | --- |
| Decachlorobiphenyl | 100 | 96.2 | 80.7 | 65.4 | 53.8 | 35.6 | 15.4 | 5.8 | < 0.1 |

*$\bar{t}_r = 1.0 \pm 0.1$ sec

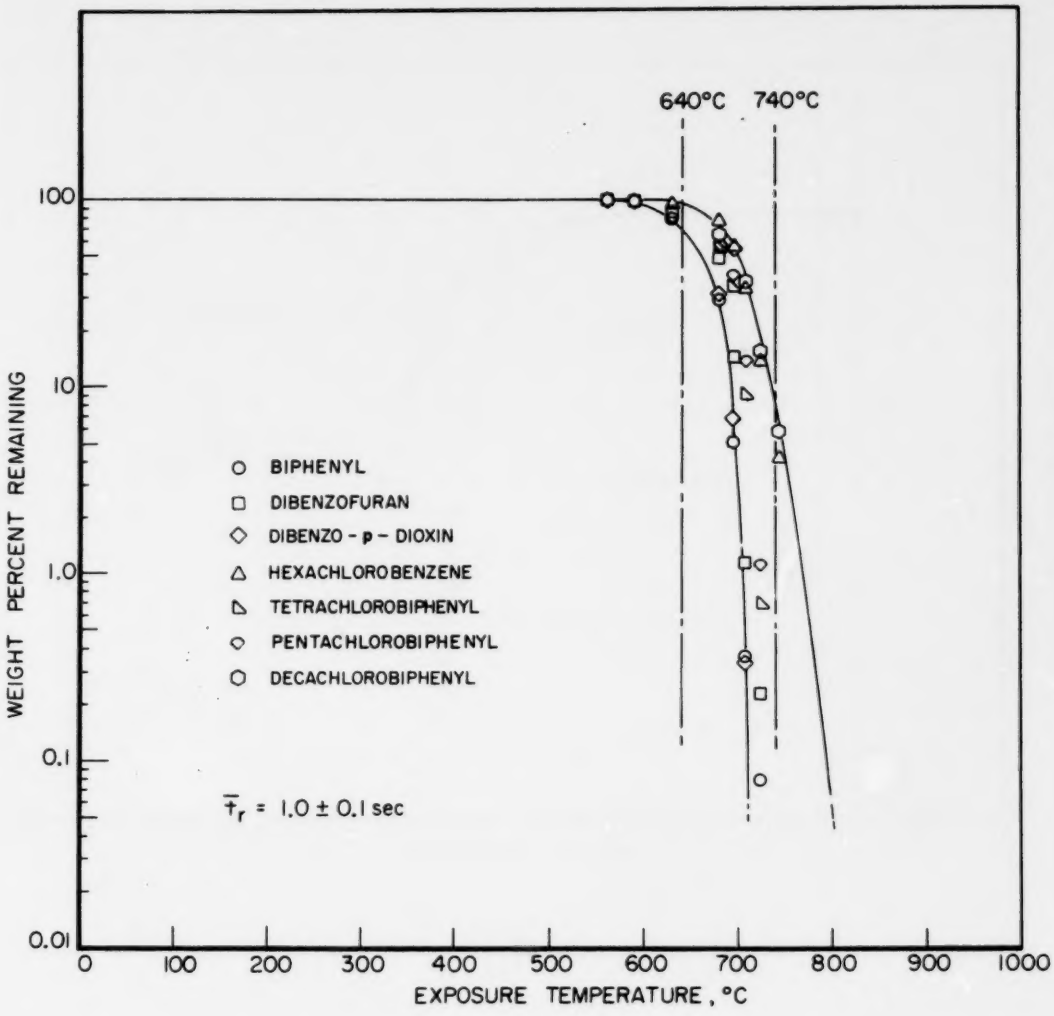



Figure 5. Scatter of thermal destruction data.

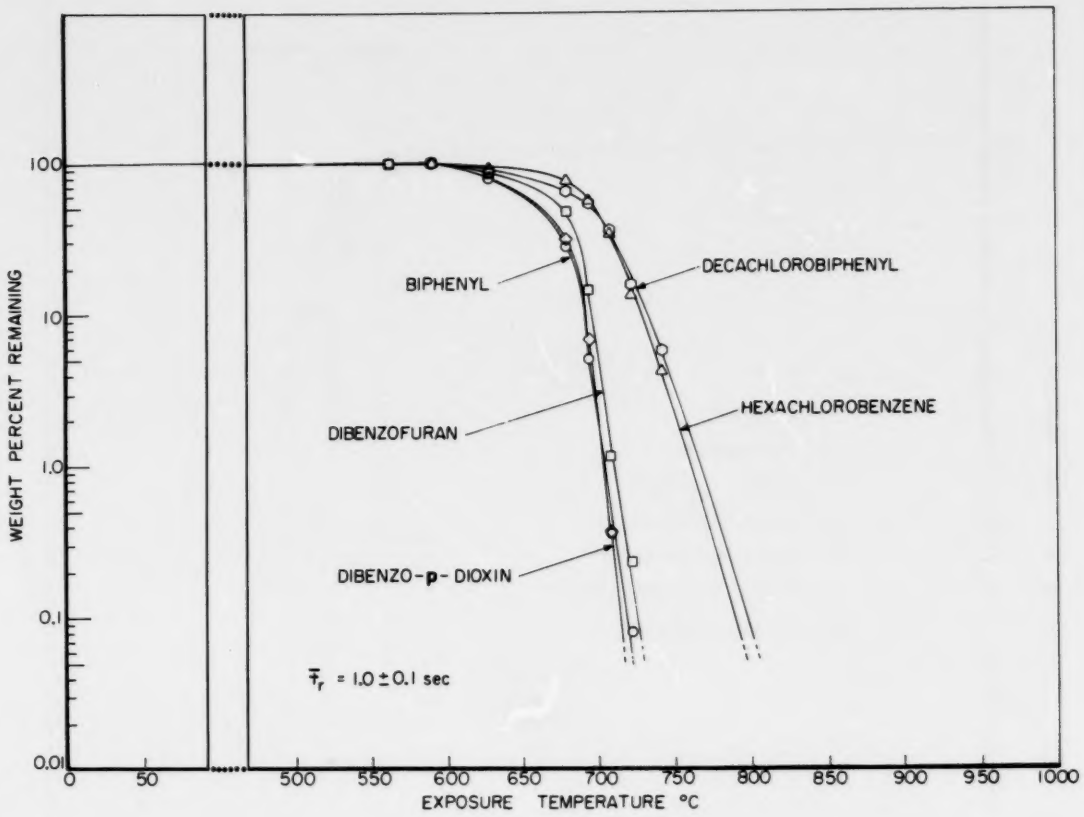



Figure 6. Thermal destruction profiles for individual compounds in the combined samples.

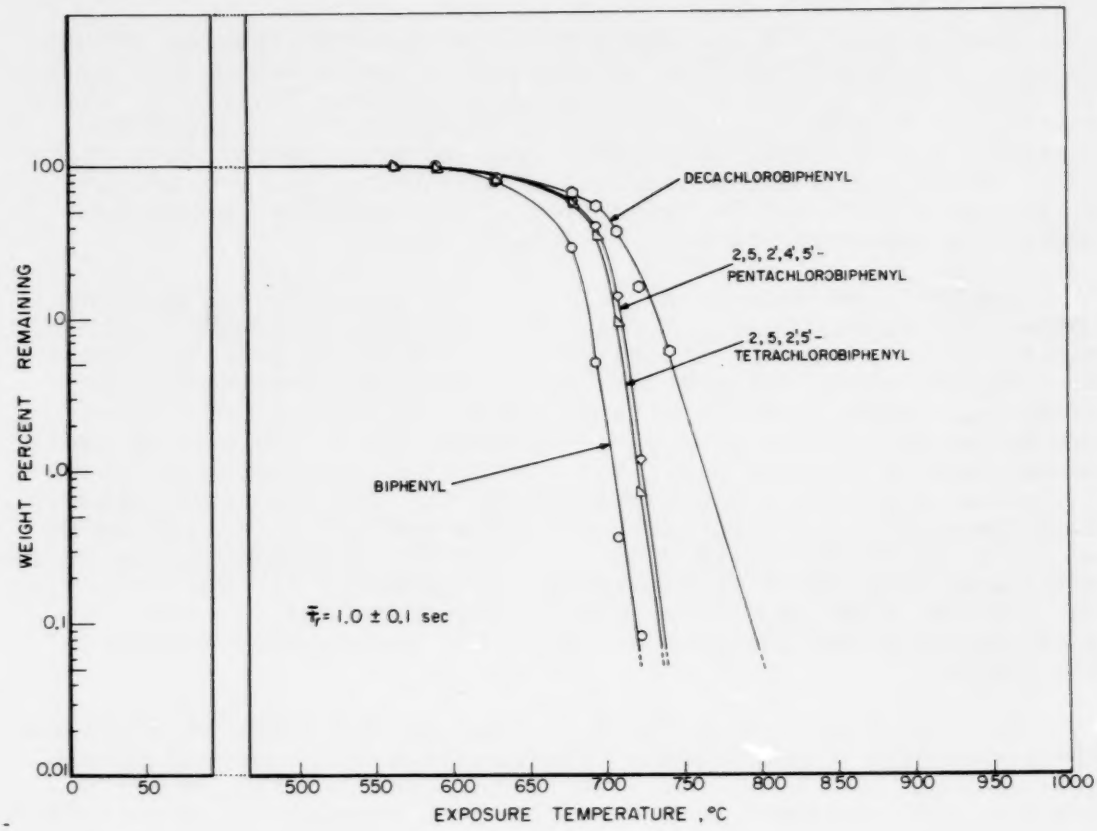



Figure 7. Thermal destruction profiles.

biphenyl has a somewhat lower thermal stability than the pentachlorobiphenyl, which in turn has a significantly lower thermal stability than the decachlorobiphenyl.

## EXAMINATION OF COMMERCIAL PCB MIXTURES

In Figure 5, it was observed from the distribution of the thermal decomposition data points that a temperature zone covering these data points is surprisingly narrow. Therefore, it was decided to assign a low-temperature threshold to signify the initiation of thermal breakdown, and an upper temperature value which would represent practical completion of the thermal destruction of PCB's (<5% remaining). The values selected for these two temperatures were 640°C and 740°C.

Each of the commercial PCB mixtures was then examined at these two temperatures. First, 40 microgram samples of each of the Aroclor mixtures were analyzed by injecting onto the Tenax-GC trapping media and conducting a programmed temperature GC analysis. Then, samples of each of the seven mixtures were subjected to a thermal exposure of 640°C for a one-second residence time in flowing dry air. Finally, each mixture was subjected to one-second exposures of 740°C. The trapped effluents from these thermal exposures were subsequently subjected to GC analysis as described in Figure 4, and the chromatographic traces resulting from these examinations are shown in Figures 8 through 14. (Note that in this series of chromatograms, signal amplification was adjusted according to hydrocarbon content of the PCB's).

In almost all cases there is very little difference between the respective chromatograms obtained from the unheated sample and the same Aroclor mixture which had been exposed to 640°C. However, the chromatograms obtained from samples exposed to 740°C, in all cases, show either an absence of chromatographic peaks, or an occurrence of peaks at locations other than what would be representative of that particular PCB mixture. (The newly-formed substances were not identified during this program). From this information it is highly probable that the thermal stability of all of the PCB compounds would fall between the extremes as depicted in Figure 5; that is bounded by the thermal destruction behaviors of biphenyl and decachlorobiphenyl.

## THERMAL STABILITY COMPARISON OF PCB's AND MIREX

Although the various PCB compounds thermally decompose within a fairly narrow region, as a group they possess considerable high-temperature stability. For comparison, the thermal destruction profile for Mirex, obtained in a previous study [42], was redrawn and directly compared with a thermal destruction plot of a representative PCB, 2,5,2',4',5'-pentachlorobiphenyl. The profiles of Mirex and this PCB are shown in Figure 15. It is

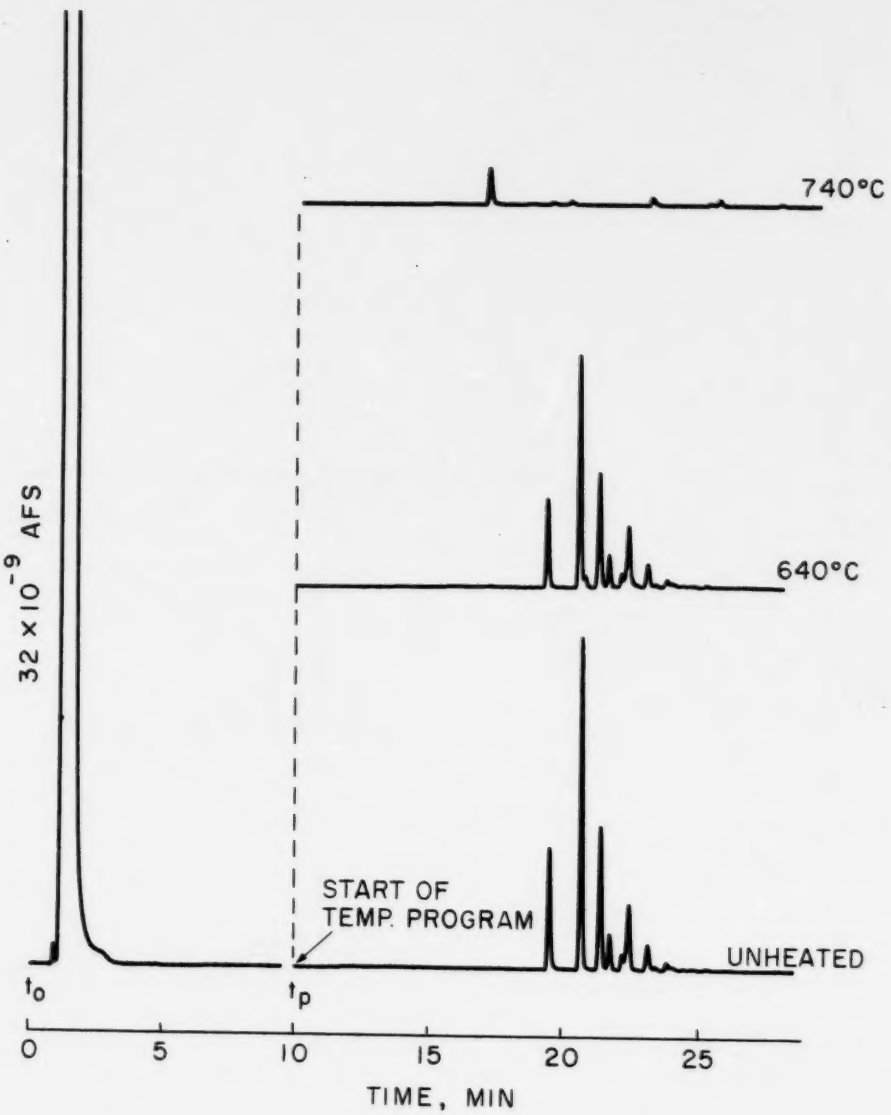



Figure 8. Chromatograms produced by Aroclor #1221 samples.

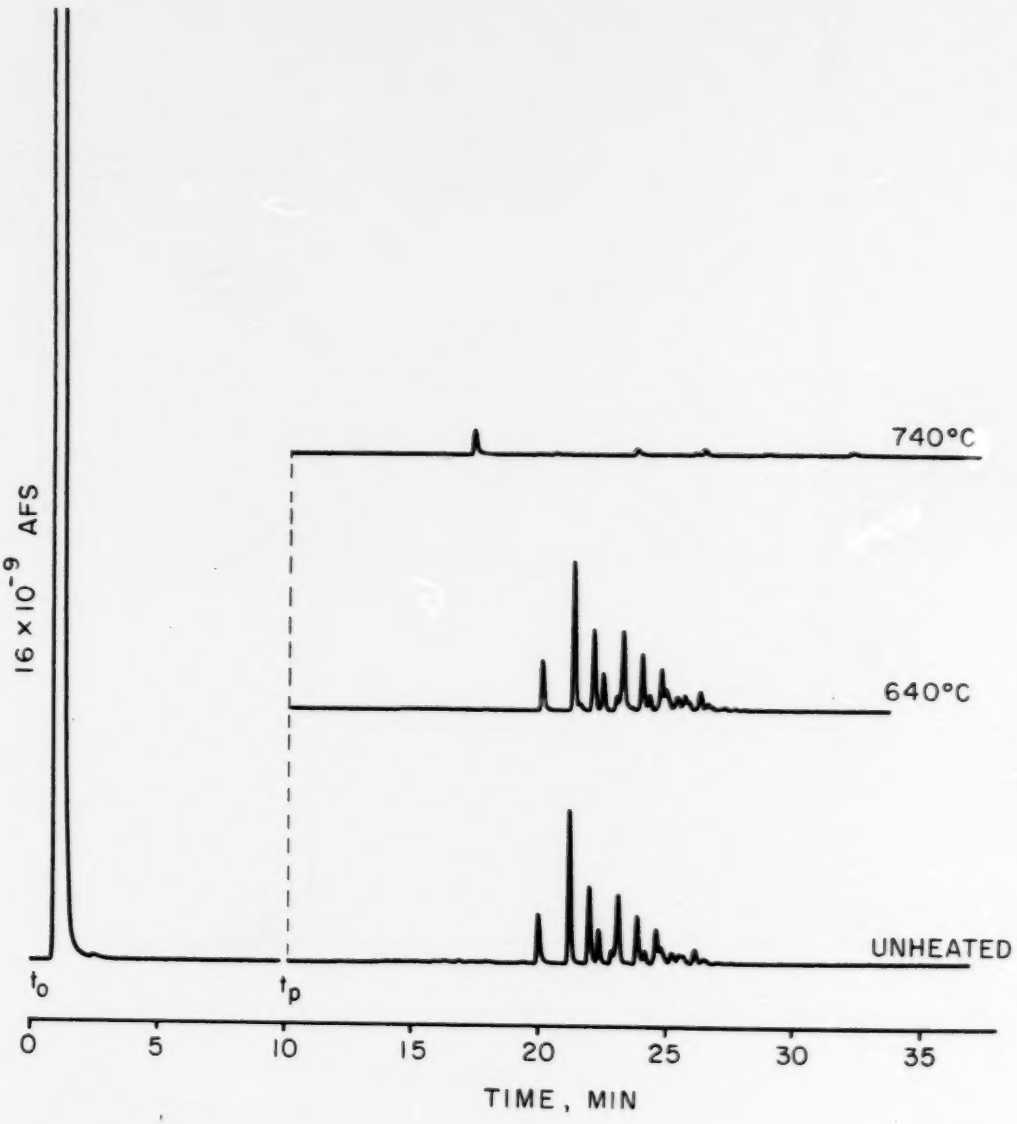



Figure 9. Chromatograms produced by Aroclor #1232 samples.

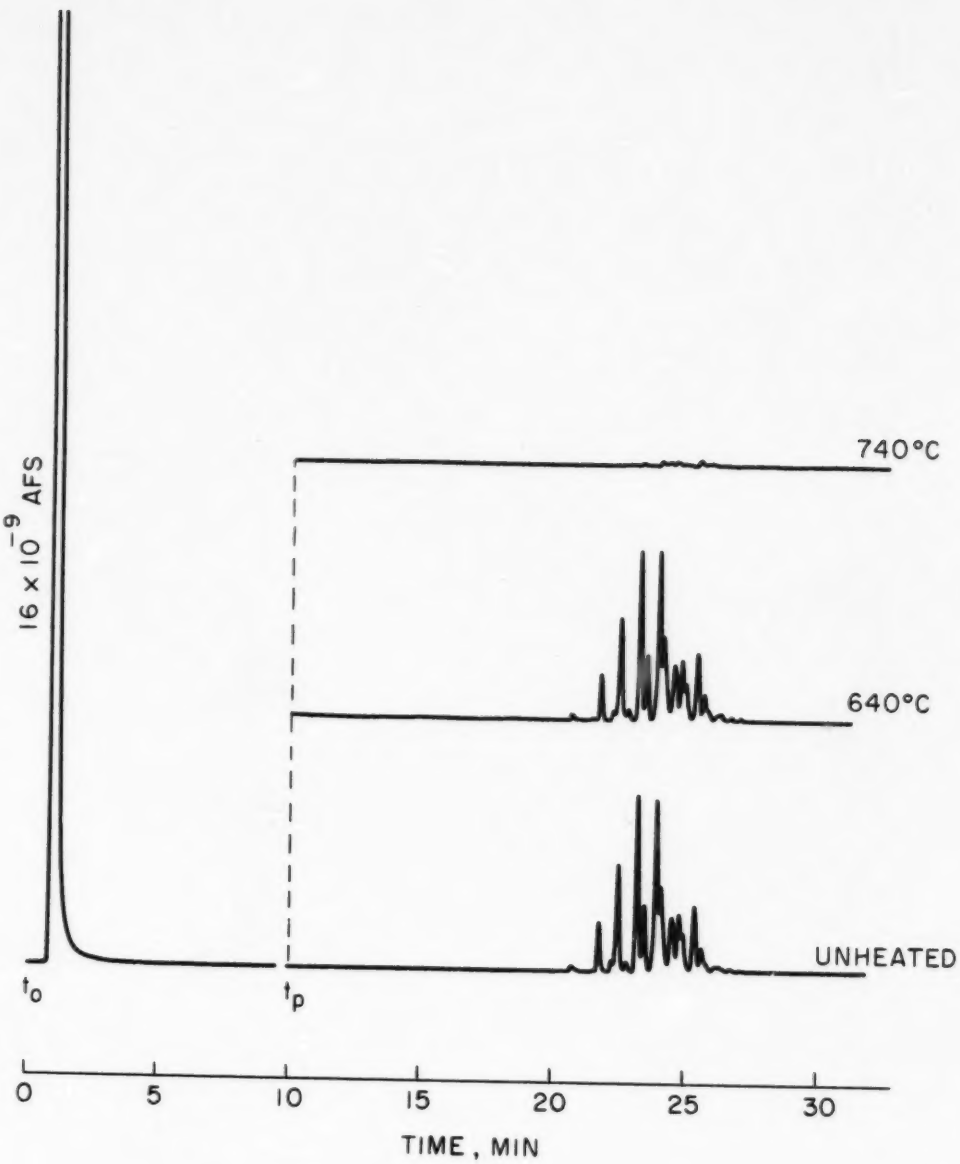



Figure 10. Chromatograms produced by Aroclor #1242 samples.

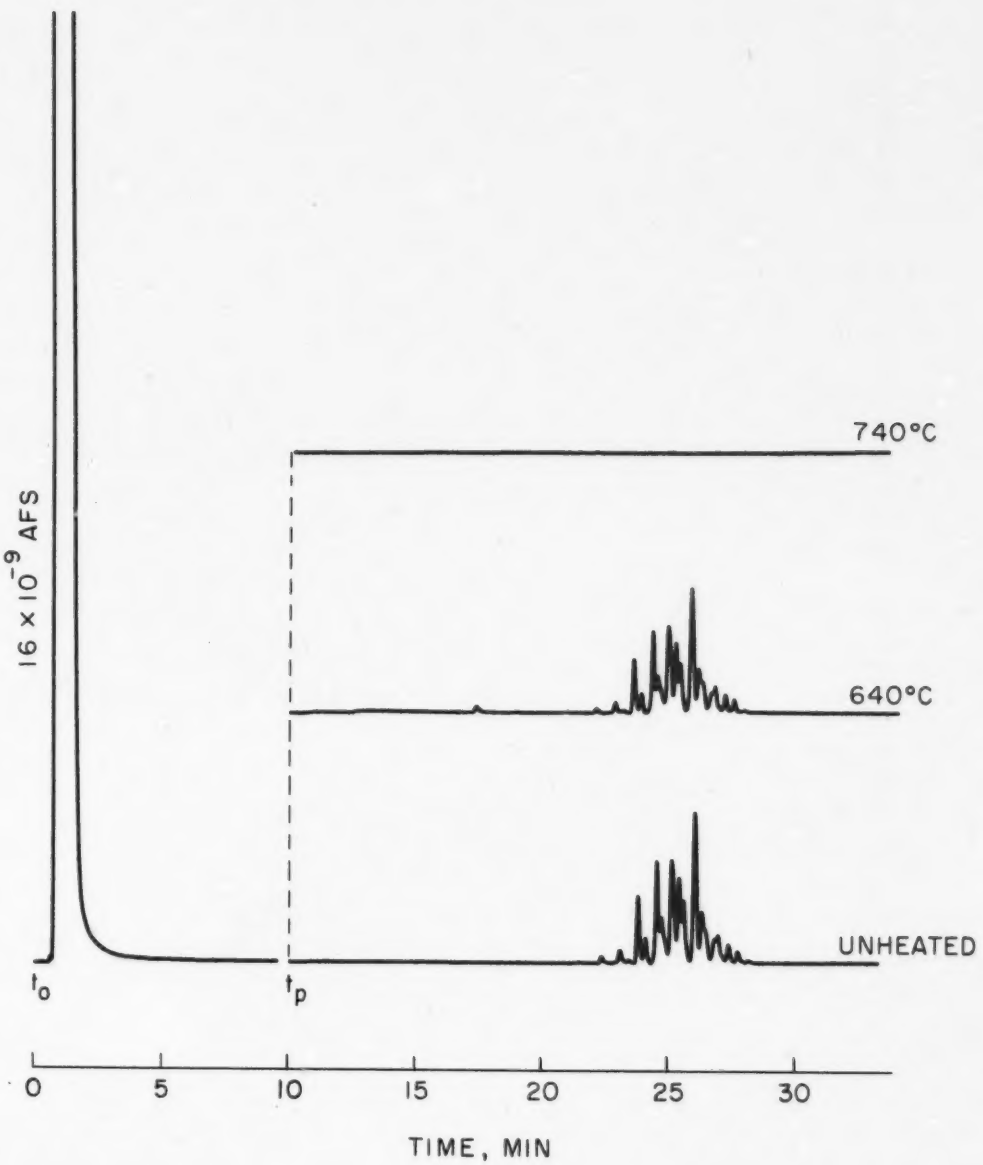



Figure 11. Chromatograms produced by Aroclor #1248 Samples.

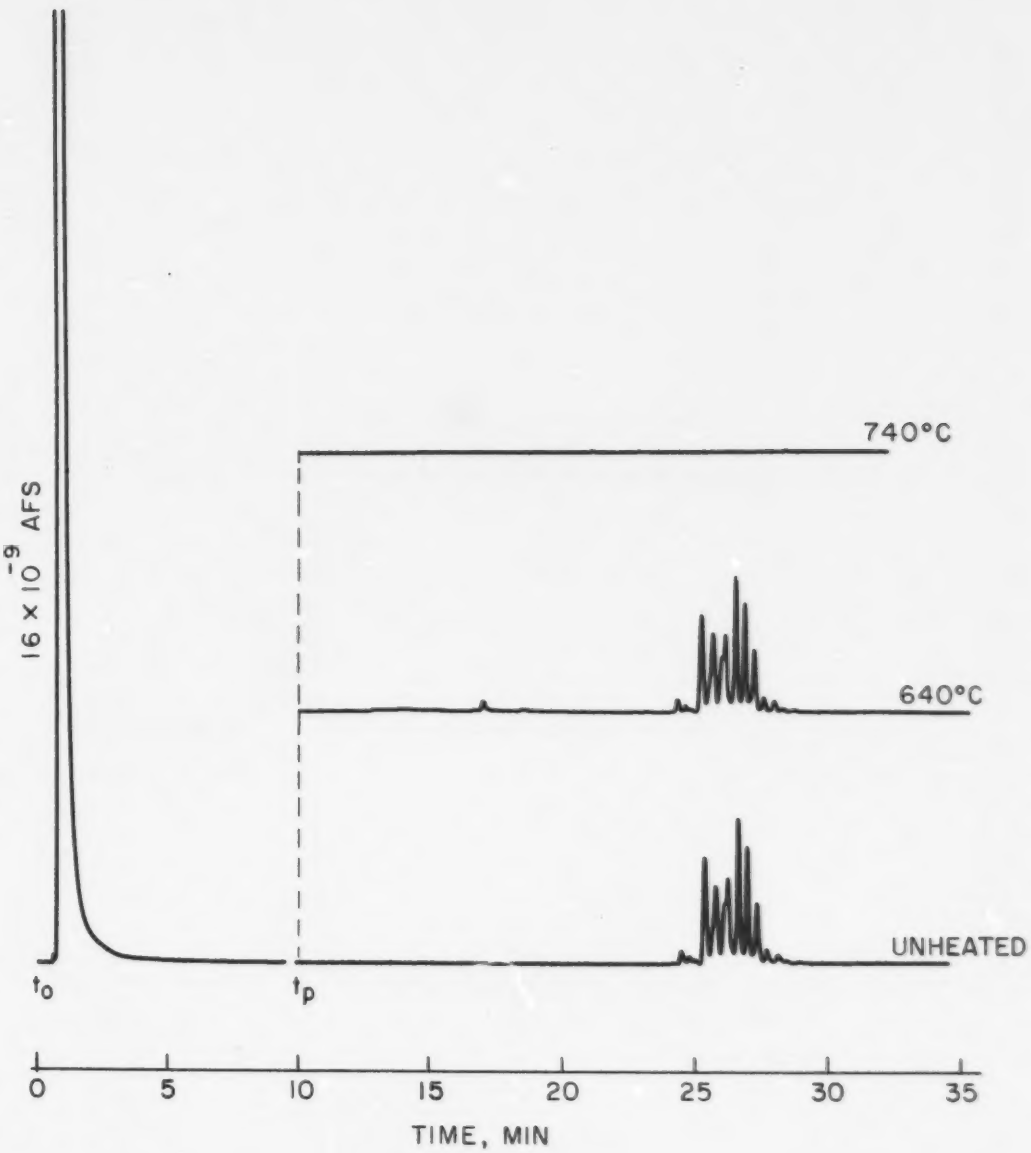



Figure 12. Chromatograms produced by Aroclor #1254 samples.

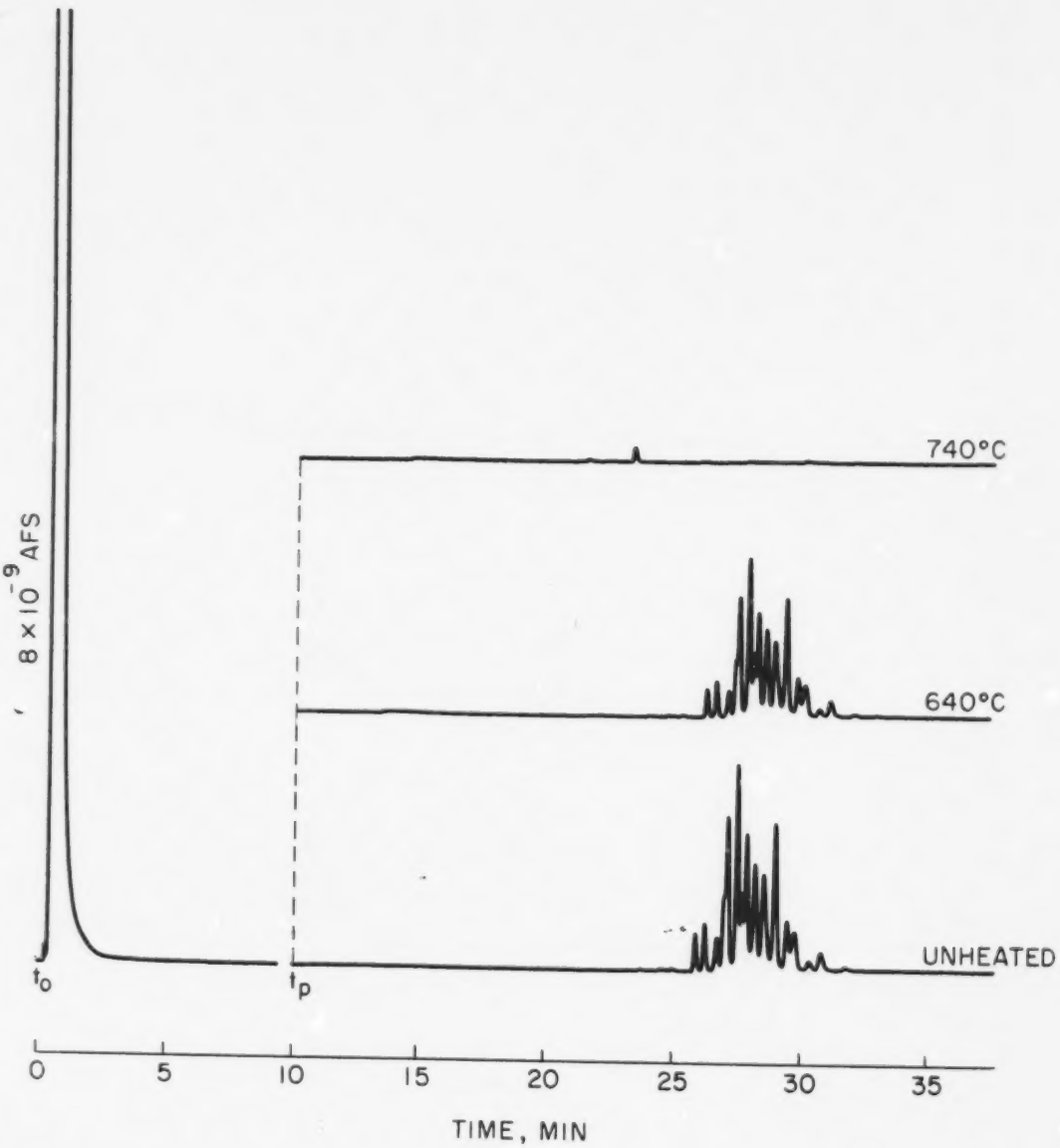



Figure 13. Chromatograms produced by Aroclor #1260 samples.

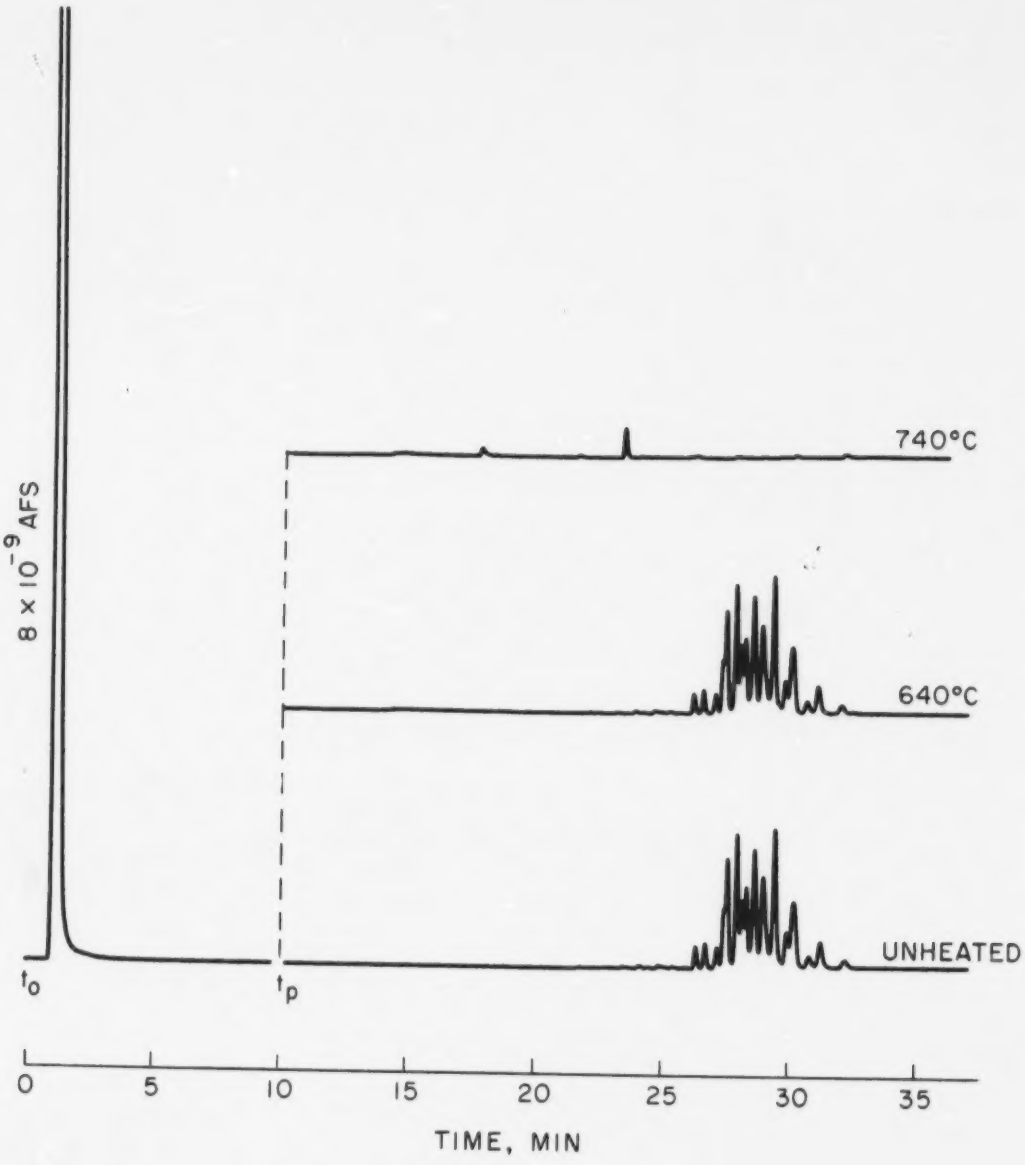



Figure 14. Chromatograms produced by Aroclor #1262 samples.

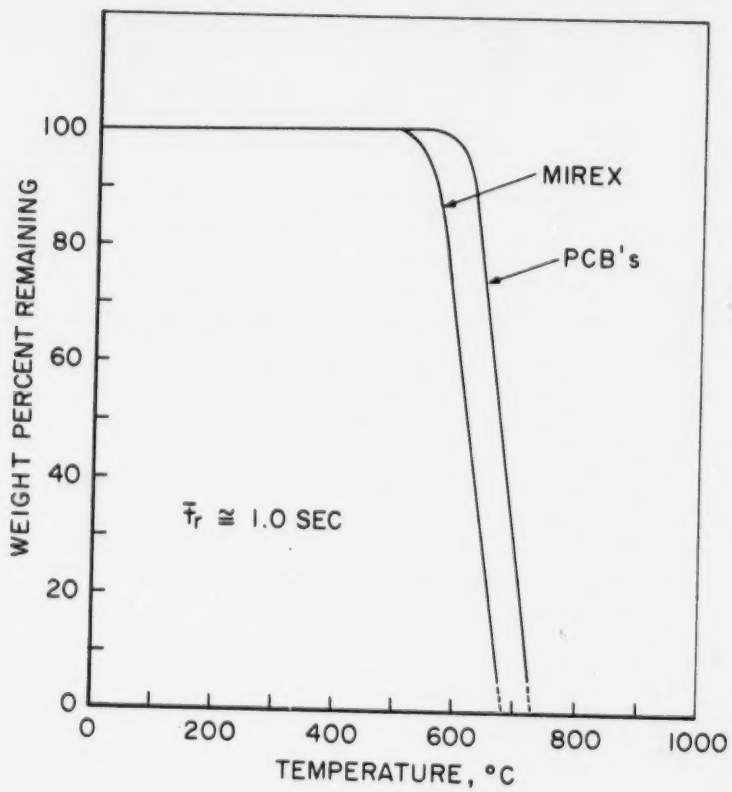



Figure 15. Comparison of thermal destruction of Mirex and PCB's.

readily apparent from this figure that PCB's are indeed considerably more stable than Mirex at high temperatures.

In addition, Mirex has also been examined by other investigators using pilot-scale incineration equipment [43]. With this high-temperature disposal equipment it was difficult to satisfactorily incinerate Mirex at temperatures of 900-1000°C. Based upon our experimental information, the thermal disposal of PCB's should require more severe thermal exposures than Mirex.

## THERMAL FRAGMENTATION OF PCB's

In an attempt to obtain a more thorough understanding of the actual thermal decomposition of PCB's, a test was conducted where a sample of Aroclor #1242 was subjected to a 690°C thermal exposure for one second. This test produced approximately 50% destruction of the Aroclor sample. A second test was conducted using the same Aroclor #1242 sample and thermal exposure conditions; however, this time a charcoal trap was substituted for the Tenax-GC trap. The contents of the charcoal trap were then chemically desorbed using carbon disulfide. This desorbed sample was first subjected to a gas chromatographic analysis which centered attention on the molecular weight range of 78 (benzene) to 189 (monochlorinated biphenyl). It was determined from this analysis that the desorbed sample contained only very low levels of organic compounds falling within the above molecular weight range. Next, the same sample was subjected to a controlled evaporation of the solvent, after which the residue was dissolved in n-hexane and subjected to a gas chromatographic analysis using a high-resolution glass open tubular column [44]. An unheated sample of Aroclor #1242 in n-hexane was also subjected to the same GC analysis. The gas chromatographic conditions for these two analyses are presented in Figure 16, while Figure 17 shows the chromatograms obtained. The chromatogram shown in Figure 17a represents the unheated Aroclor #1242; Figure 17b represents the collected effluent from an equal quantity of Aroclor #1242 that was subjected to a 690°C, one-second thermal exposure in air. Essentially, both samples contain the same compounds. However, through comparison of the normalized integrated responses, it was again determined that approximately 50% of the heated Aroclor #1242 was thermally decomposed. Upon numerical comparison of the individual peaks in these two chromatograms, it was generally found that proportionally more of the lower molecular weight PCB compounds decomposed than the higher molecular weight compounds.

The main conclusion derived from this thermal testing of Aroclor #1242 in air is that PCB compounds fragment to low molecular weight products, generally lighter than benzene, upon reaching a destructive temperature. This same type of fragmentation was obtained through another series of high-temperature destruction tests, the results of which are illustrated in

GAS CHROMATOGRAPHIC CONDITIONS

| | | |
|---|---|---|
| Instrument | Varian 1860-1 | |
| Analyst | W. Rubey | |
| Date | Aug. 12, 1977 | |
| Column: | | |
| tubing material | soft glass | |
| tubing length | 15 | meters |
| tubing bore | 0.25 | mm |
| Stationary Phase | SE-30 Silicone | |
| weight | --- | |
| Support | --- | |
| mesh | --- | |
| Carrier Gas | Helium | |
| inlet pres | 1.9 | abs atmo |
| linear velocity | 20 | cm/sec |
| outlet flow | ∿0.6 | ml/min |
| Chart Advance | 1.0 | cm/min |
| Read Out | 1.0 | mv full scale |
| Sample | Aroclor 1242 | |
| size | 5.0 µl | |
| Detector | HFlD | |
| range | $10^{-11}$ | |
| attenuation | 8 | |
| Gas Flows, ml/min | | |
| hydrogen | 30 | |
| air | 300 | |
| split ratio | 45 to 1 | |
| Temperatures, °C | | |
| detector | 290 | |
| injector | 260 | |
| column: | | |
| initial | 100 | |
| final | 230 | |
| program rate | 4.0 | °C/min |
| Sample Solvent | n-hexane | |
| concentration | 0.8 µg/µl | |

Figure 16. Open tubular column gas chromatographic conditions.

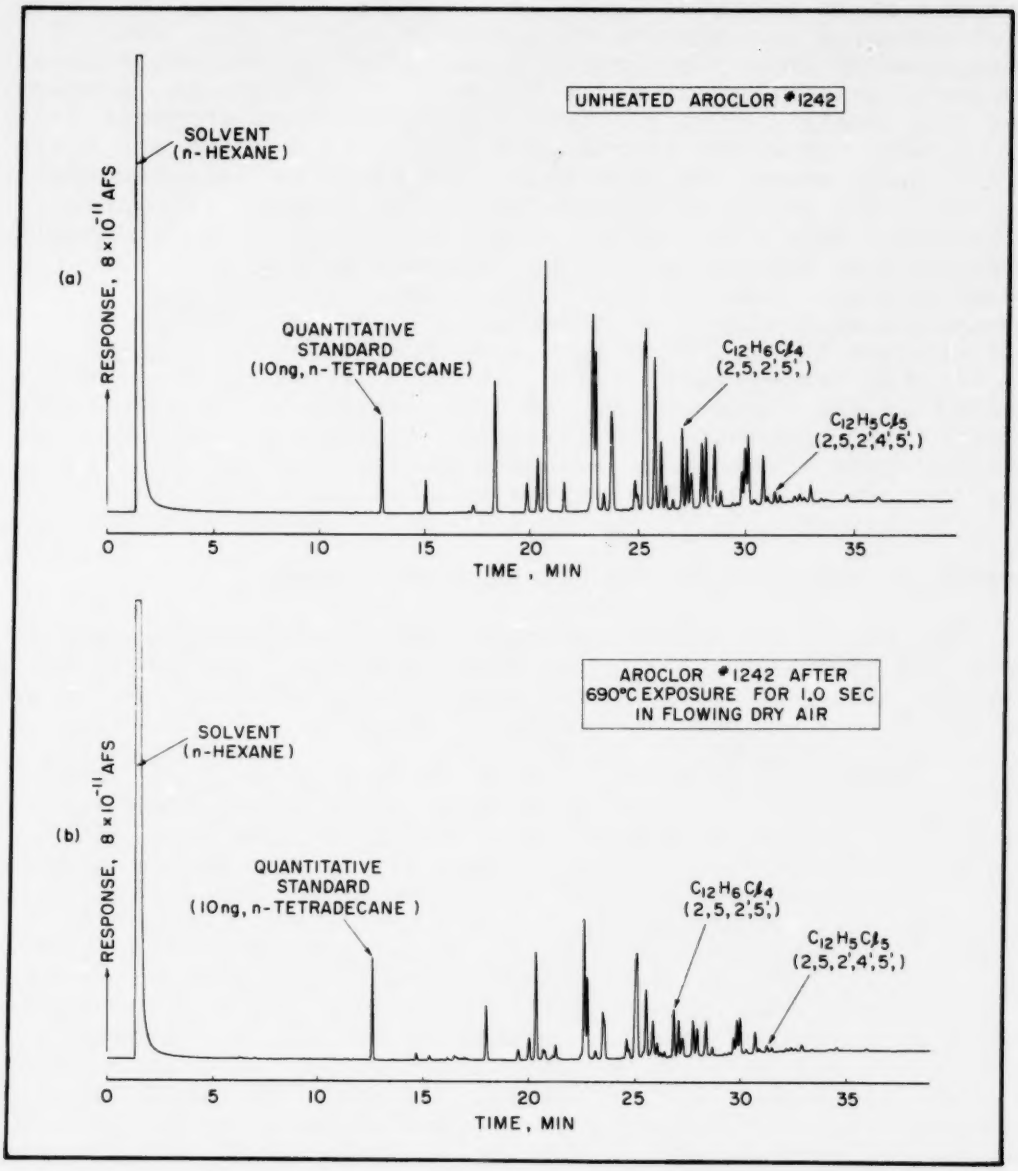



Figure 17. Chromatograms of Aroclor #1242 samples.

Figure 18. The bottom GC trace represents the chromatographic analysis of an unheated 2,5,2',4',5'-pentachlorobiphenyl sample, which contains an impurity of approximately 0.25%. When 40 micrograms of this substance are subjected to thermal exposure at increased temperatures, e.g., those in Figure 18, it is observed that only small levels of trapped decomposition products (<1%) are formed. (The PCB isomer peak was allowed to go off-scale during these tests, so that attention could be centered upon the decomposition products formed during the thermal exposures.) It is apparent from this series of chromatograms that decomposition products that can be trapped by Tenax-GC are of very low concentration. Despite their low level, the same pattern of decomposition products is observed at exposure temperatures of 651° through 727°C. When this same PCB isomer is exposed to an even higher temperature, 754°C, the PCB isomer is no longer present in the chromatogram and only extremely low levels of decomposition products are observed. Again, the information obtained from these tests agrees with the earlier results, i.e., once the PCB molecule encounters a thermally destructive environment, it essentially fragments into small decomposition products.

## THERMAL DESTRUCTION AT THE HIGHER TEMPERATURES

The extent of thermal destruction at temperatures above 800°C was next investigated in this laboratory program. Subsequently, a sample was prepared which contained equal parts by weight of each of the seven Aroclor mixtures and the 2,5,2',4',5'-pentachlorobiphenyl. (A chromatogram of this composited sample, dissolved in hexane, is shown in Figure 19.) High-temperature exposure tests were then conducted at 900°C and 1000°C with a mean residence time of 1.0 seconds. An additional test was performed at 1000°C using a 2.0 second mean residence time. The respective trapped effluents were then analyzed. By using the peak height of the pentachlorobiphenyl isomer as a quantitative measure, destruction percentages for these high-temperature exposures were calculated and tabulated in Table II. It is evident that increased residence time has a pronounced effect upon the destruction percentage at 1000°C. Another observation was made while analyzing the chromatograms produced by this composited Aroclor sample. It was noted that the lower molecular weight PCB compounds, those emerging to the left of the pentachlorobiphenyl in Figure 19, were almost totally absent in the collected effluents. However, traces of the heavier PCB's, those with retention times to the right of the pentachlorobiphenyl, were still in evidence after the 1000°C exposure. Thus, this would again substantiate the finding that the higher the molecular weight of a PCB, the greater its thermal stability.

## RESIDENCE TIME CONSIDERATIONS.

To further examine the effect of residence time, tests were conducted at a fixed temperature which was less than required

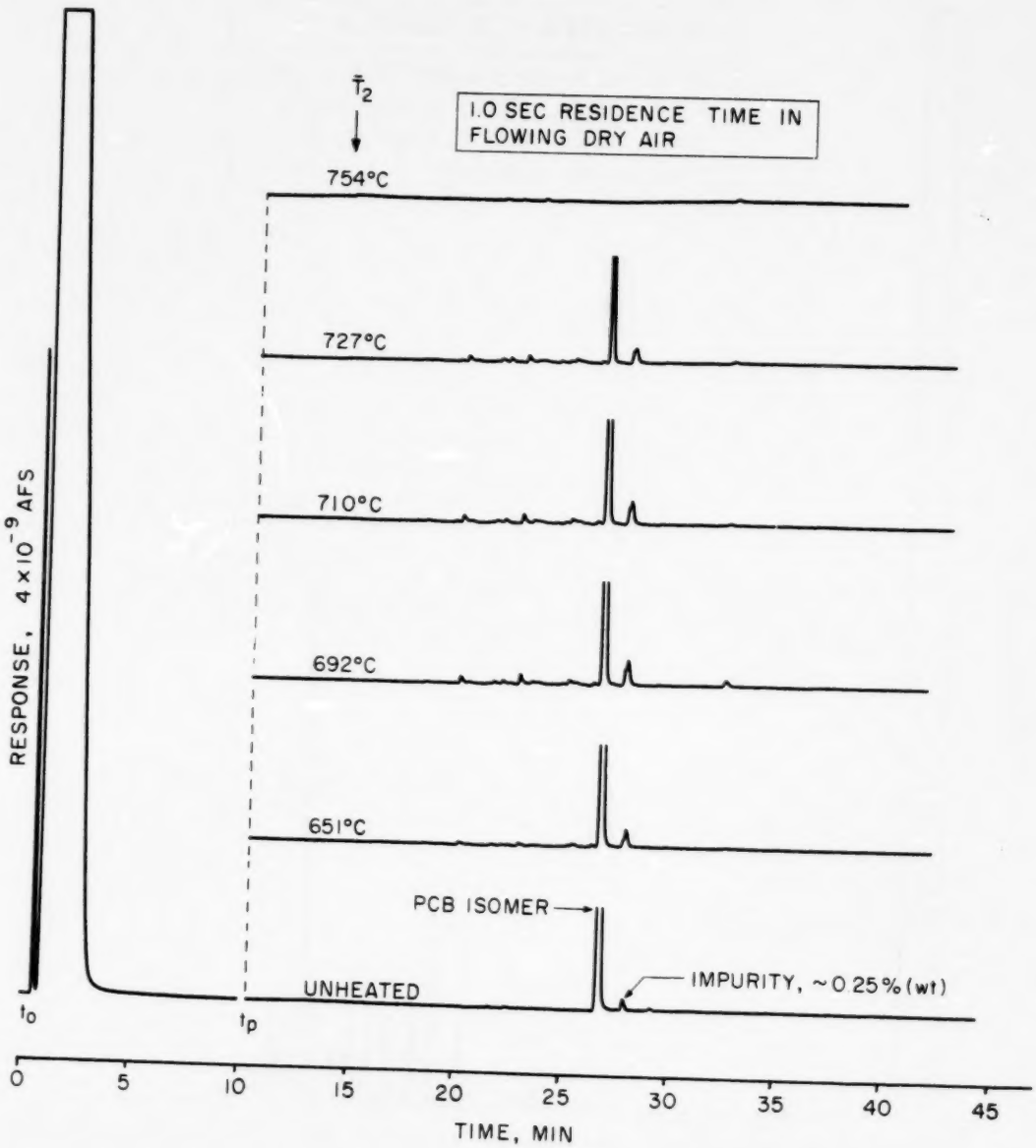



Figure 18. Chromatograms of 2,5,2',4',5', - pentachlorobiphenyl samples.

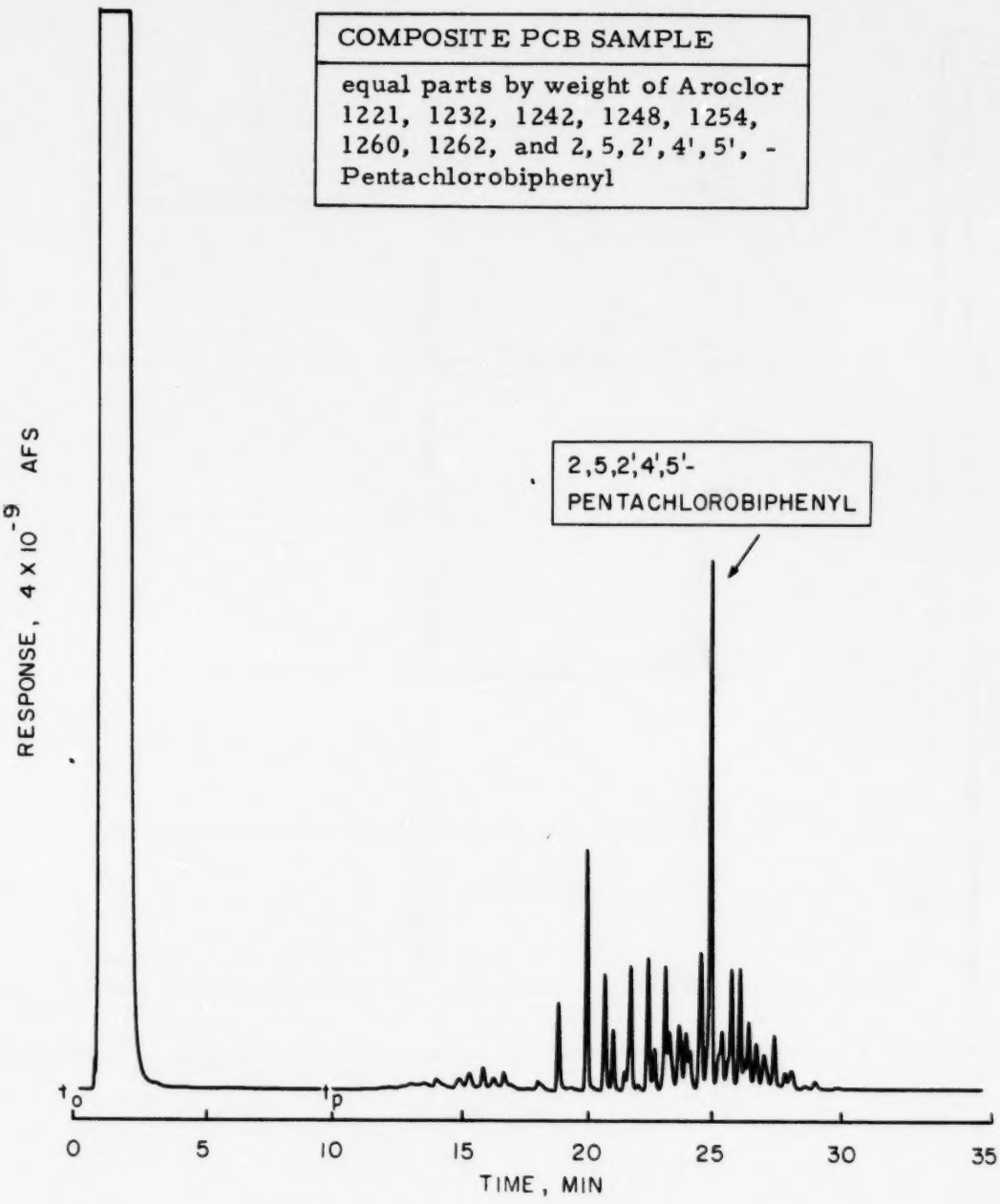



Figure 19. Chromatogram of composited Aroclor mixtures plus 2,5,2',4',5', - pentachlorobiphenyl.

TABLE II. HIGH-TEMPERATURE EXPOSURE DESTRUCTION PERCENTAGES

| Exposure Temperature, $\bar{T}_2$ (°C) | Residence Time, $\bar{t}_r$ (sec) | Destruction Percentage* |
|---|---|---|
| 900 | 1.0 | 99.988 |
| 1000 | 1.0 | 99.995 |
| 1000 | 2.0 | 99.9995 |

*Destruction Percentage = $100 \left[1 - \left(\frac{\text{wt trapped sample}}{\text{wt input sample}}\right)\right]$

TABLE III. WEIGHT PERCENT REMAINING AFTER 704°C EXPOSURE FOR RESPECTIVE RESIDENCE TIMES

| Compound | Residence Time, Sec | | |
|---|---|---|---|
| | 0.27 | 0.95 | 3.84 |
| Biphenyl | 8.1 | 0.70 | 0.07 |
| Dibenzofuran | 35.1 | 3.8 | 0.93 |
| Dibenzo-p-dioxin | 45.3 | 1.2 | 0.07 |
| Hexachlorobenzene | 88.4 | 37.2 | 11.3 |
| Tetrachlorobiphenyl (2, 5, 2', 5') | 78.5 | 14.0 | 2.6 |
| Pentachlorobiphenyl (2, 5, 2', 4', 5') | 81.1 | 18.5 | 3.4 |
| Decachlorobiphenyl | 84.7 | 37.3 | 16.1 |

for complete thermal decomposition. Specifically, a combined sample containing pure compounds was examined using a 704°C exposure, but with different air flow rates passing through the quartz-tube apparatus, thereby obtaining different residence times at the fixed temperature. The effluent samples obtained at these different residence times were then analyzed. The results are presented in tabular form in Table III. These same data are presented in log-log form in Figure 20. From these data, it is readily apparent that residence time is a very strong factor affecting the high-temperature destruction of PCB's and related compounds.

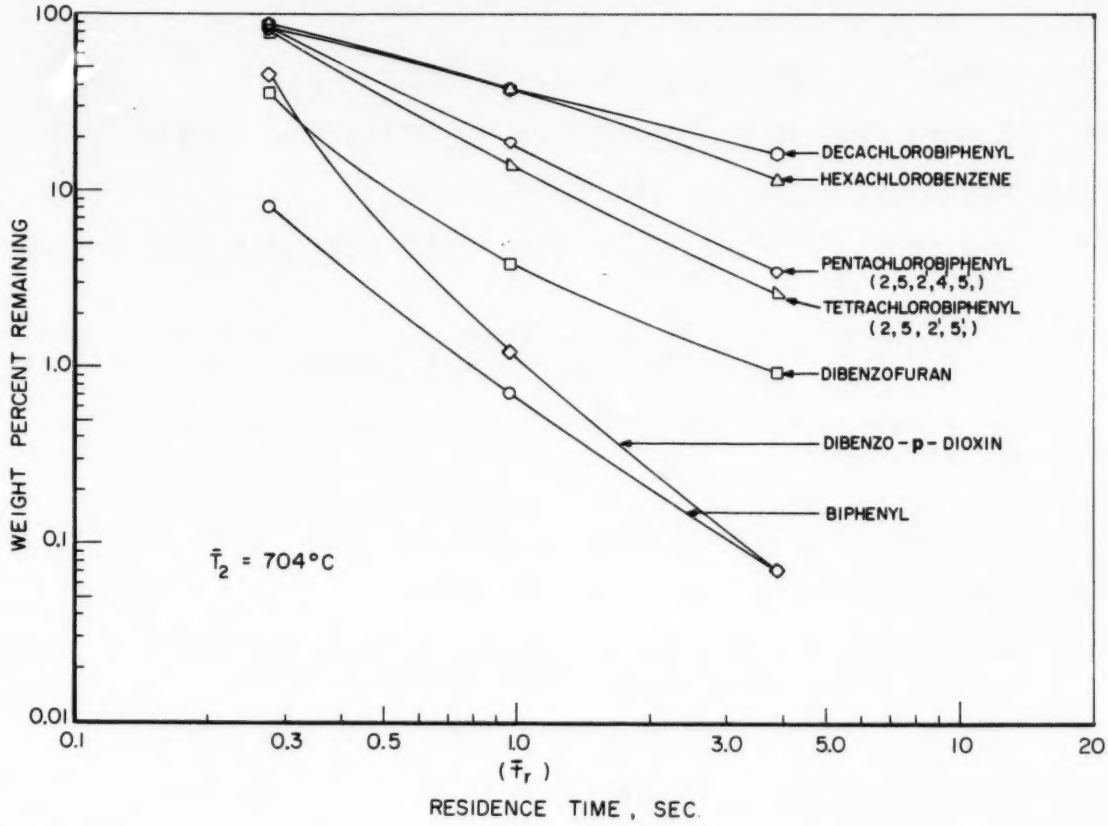



Figure 20. Effect of residence time at 704°C.

## REFERENCES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## APPENDIX I

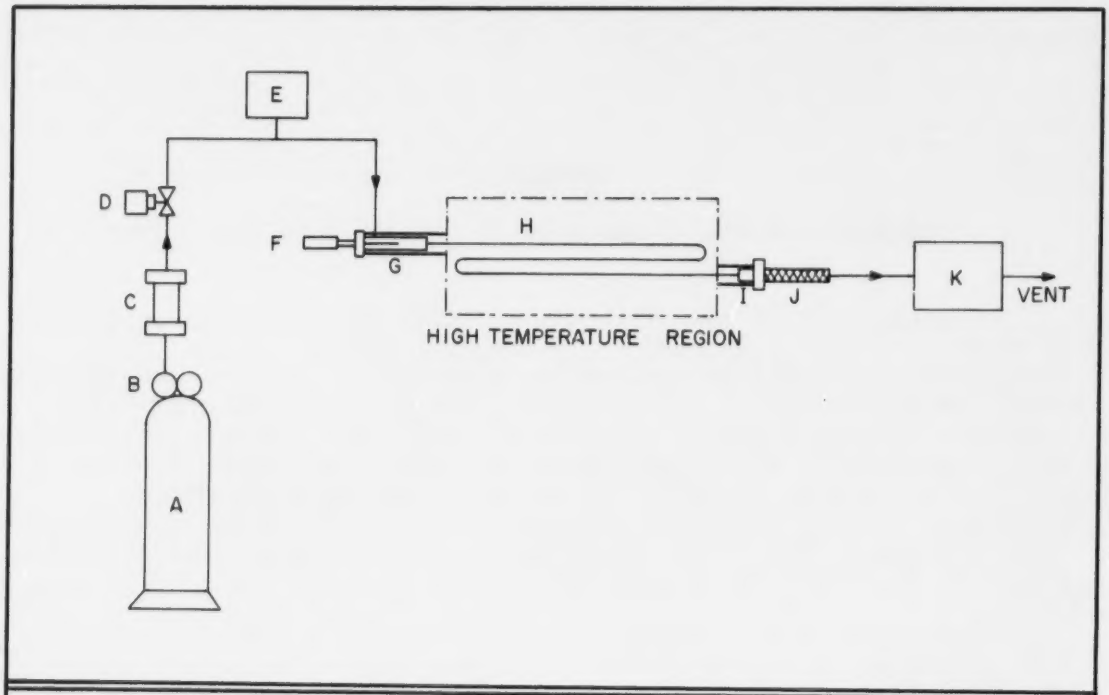
## DESCRIPTION AND OPERATION OF QUARTZ TUBE APPARATUS

A schematic of the high-temperature quartz tube apparatus is shown in Figure A1, and a photograph in Figure A2. An important component in this apparatus is the folded quartz tube which is contained in a Lindberg furnace, type 55035A. Two separate quartz tubes of different bore size are available with this apparatus. Both tubes have an effective length, when positioned in the furnace, of 84 cm. The average inside diameters of the finished, folded tubes are 0.80 mm and 2.14 mm, respectively. The study reported on here made principle use of the 0.80 mm inside diameter folded tube.

Upstream of the installed, folded quartz tube is a special sample holder which is shown in Figure A3a. Using a 10 microliter syringe and following suggested procedures [45], a known quantity of diluted sample can be readily deposited on the sand blasted region of the sample holder. The solvent quickly evaporates, leaving the sample on the rough Pyrex surface. This device is then inserted into a chamber upstream of the high-temperature quartz tube. Next, this chamber is gradually heated to the extent necessary to vaporize the sample, thereby sweeping the gas phase molecules through the high-temperature tube.

An effluent trap is located at the outlet of the high-temperature tube. A sketch of the basic trap is shown in Figure A3b. This long Pyrex tube (22.5 cm) is connected to the quartz tube outlet with a special Swagelok reducer union containing a Teflon sleeve. Vespel ferrules were used to produce a gas-tight seal. The outlet of the trapping medium tube approaches ambient temperature.

A variety of different trapping media can be used for collecting organic products. Of special interest, however, is Tenax-GC, which has been found to be an excellent trapping medium for various organic compounds and their respective decomposition products (M.W. of 150 to 550). Tenax-GC, a porous polymer, is commercially available in 35/60 and 60/80 mesh sizes. Also, this material has a desirable feature in that it can be readily, thermally desorbed [46-53]. The research reported on here utilized traps prepared with the 60/80 mesh Tenax-GC




A. COMPRESSED AIR, BREATHING QUALITY GRADE

B. TWO STAGE PRESSURE REGULATOR

C. "HYDROPURGE" FILTER

D. FLOW CONTROL VALVE

E. PRESSURE TRANSDUCER

F. SAMPLE HOLDER, PYREX

G. HEATED INLET CHAMBER

H QUARTZ TUBE

I. HEATED OUTLET CHAMBER

J EFFLUENT TRAP, TENAX-GC OR CHARCOAL

K FLOW METER

Figure A1. Schematic of quartz tube apparatus.

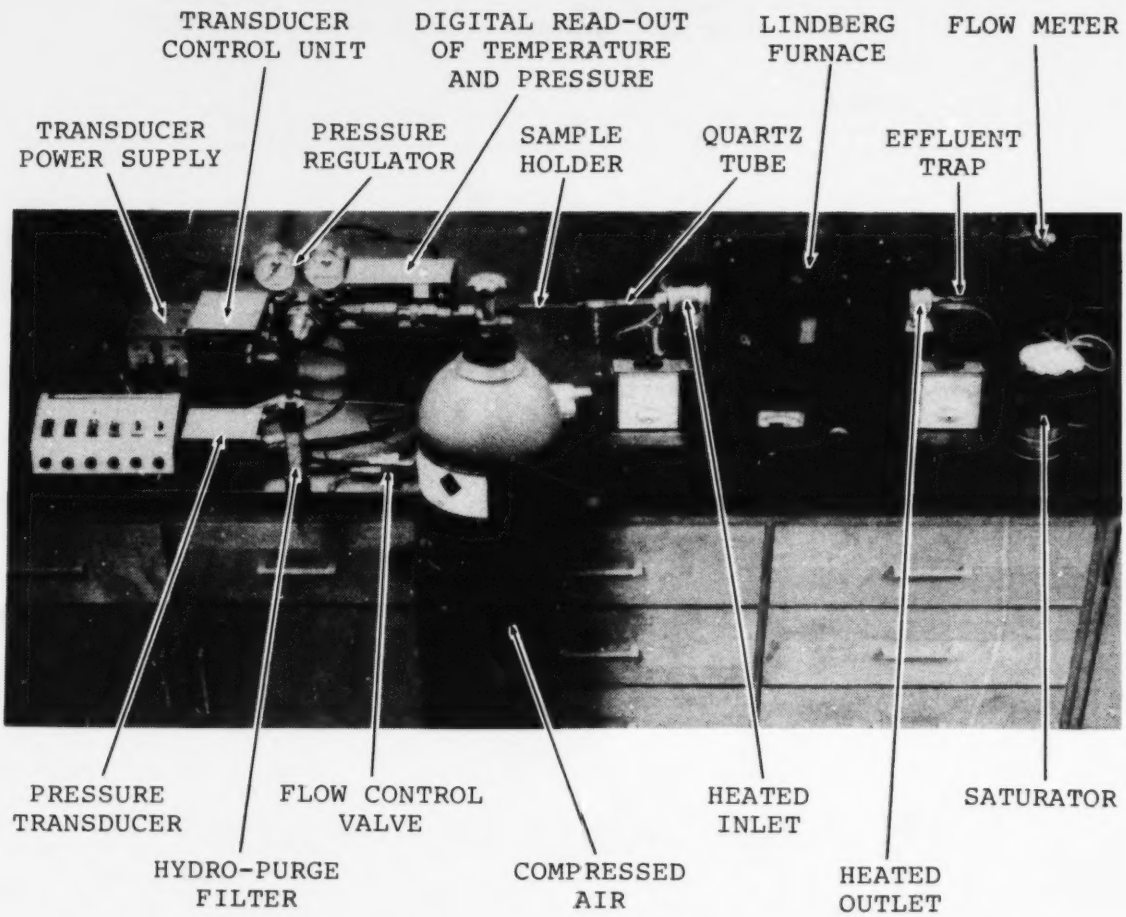
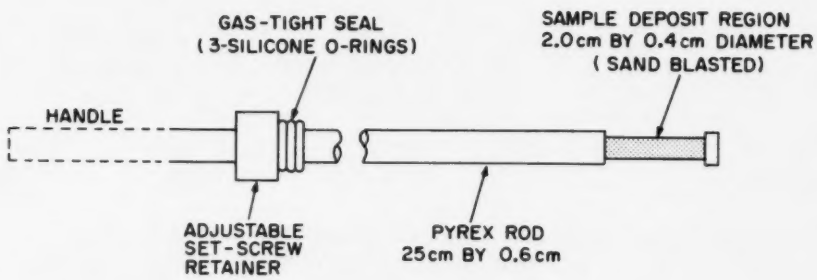
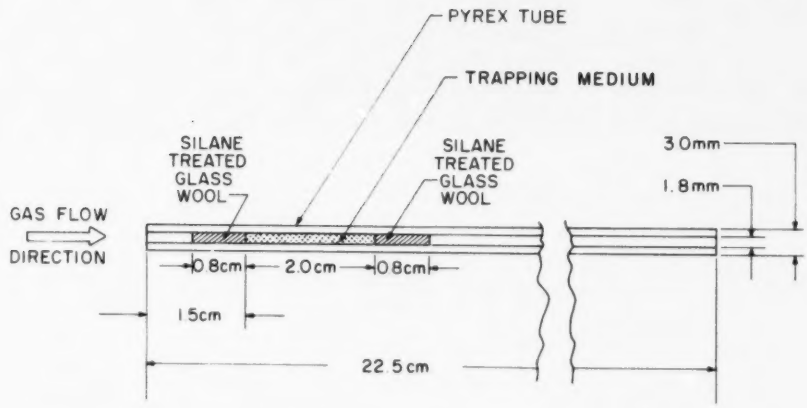



Figure A2. Photograph of quartz tube apparatus.




(a) sample holder




(b) effluent trap

Figure A3. Sample holder and effluent trap.

particles. A 2.0 cm length of this Tenax-GC packing was sufficient to obtain quantitative recoveries of pesticides and other related organic compounds. However, acetone and benzene are not quantitatively retained at the typical trap inlet temperature of approximately 300°C. Charcoal [54,55] has also been used as a trapping medium, however, it must be chemically desorbed as opposed to the thermal desorption of Tenax-GC.

Other important components in this high-temperature destruction apparatus are a Porter flow control valve (model number VCD-1000), a differential pressure transducer, two Blue M model APH-500 temperature indicators, which continually display the temperatures of the inlet and outlet chambers, and a specially fabricated soap-bubble flowmeter for measuring the system's outlet flow rate. The gas used with this apparatus was breathing quality compressed air passed through an Applied Science Laboratories Hydro-Purge filter. The average temperature in the high-temperature furnace is continually monitored by the digital readout from a compensated chromel-alumel thermocouple.

From the sketch shown in Figure A4, it is seen that the pressures, temperatures, and volumes in this system can be related according to the ideal gas law as follows:

$$\frac{V_2 p_2}{\bar{T}_2} = \frac{V_o p_o}{T_o} \quad , \tag{A.I.1}$$

where V is volume, p is pressure, T is temperature, and $\bar{T}$ is temperature averaged over the length of the tube. The subscript $\underline{2}$ denotes the quartz tube interior, while the subscript $\underline{o}$ represents the ambient outlet conditions.

Due to the extremely low pressure drop posed by the open quartz tube, and the comparatively high pressure drop presented by the packed small particle effluent trap, the differential pressure $p_d$ can be expressed as

$$p_d = p_2 - p_o = p_1 - p_o \quad . \tag{A.I.2}$$

Now, volume flow F can be written as

$$F = \frac{V}{t} \quad , \tag{A.I.3}$$

where t is time, equation (A.I.1) can be rewritten as

$$\frac{V_2 p_2}{\bar{T}_2} = \frac{F_o t p_o}{T_o} \quad , \tag{A.I.4}$$

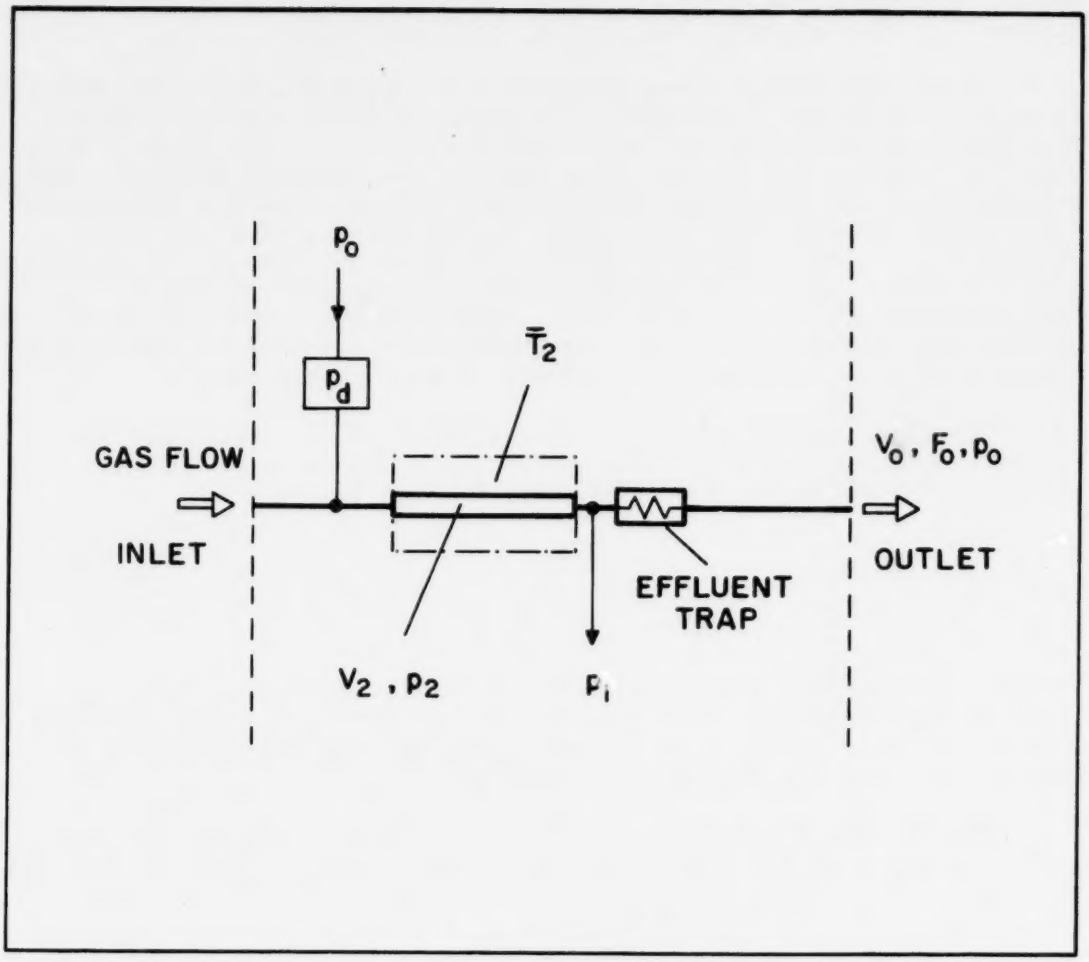



Figure A4. Sketch of pressure, volume, and temperature relationship in test system.

or

$$\frac{\pi r^2 L p_2}{\bar{T}_2} = \frac{F_o t p_o}{T_o} \quad , \qquad \text{(A.I.5)}$$

where r and L are the tube radius and length, respectively. Therefore, it is seen that time, or, in this case, residence time can be written simply as

$$\bar{t}_r = \left(\frac{\pi r^2 L}{F_o}\right)\left(\frac{T_o}{\bar{T}_2}\right)\left(1 + \frac{p_d}{p_o}\right) \quad , \qquad \text{(A.I.6)}$$

where $\bar{t}_r$ represents the calculated mean residence time of a substance in the quartz tube interior.

Special equipment is required to measure the outlet flow, the temperature of the quartz tube, and the upstream differential pressure. Specifically, the outlet flow is measured with a small bore soap-bubble flowmeter having an in-line water saturator [56]. This device was fabricated in the University Glass Shop and incorporated a calibrated volumetric pipette in the design. The average temperature of the quartz tube was determined by measuring the axial temperature profile in the Lindberg furnace and then determining the location of a point within the furnace which would represent the average temperature. This point was found to be at a location 9 cm from the axial midpoint of the furnace. The temperature profile for the contained, folded quartz tube is shown in Figure A5. This thermal information was obtained with a chromel-alumel thermocouple, which was used to measure the temperature at 1 cm increments along the tube furnace axis. The average temperature that a compound would encounter during its gas phase traverse through the quartz tube is represented by $\bar{T}_2$ as shown in Figure A5.

The pressure within the quartz tube is difficult to measure. A low pressure gage, such as a Bourdon gage, customarily exhibits high degrees of inaccuracy, along with a large mechanically induced hysteresis. Consequently, a very precise pressure transducer is used to measure the differential pressure at the inlet to the quartz tube. This pressure transducer (see Figure A6) is extremely accurate, linear, and exhibits no hysteresis. The output from the pressure transducer is displayed on a digital millivoltmeter. The system differential pressure varies with the particle size of the trapping medium and the linear gas velocity.

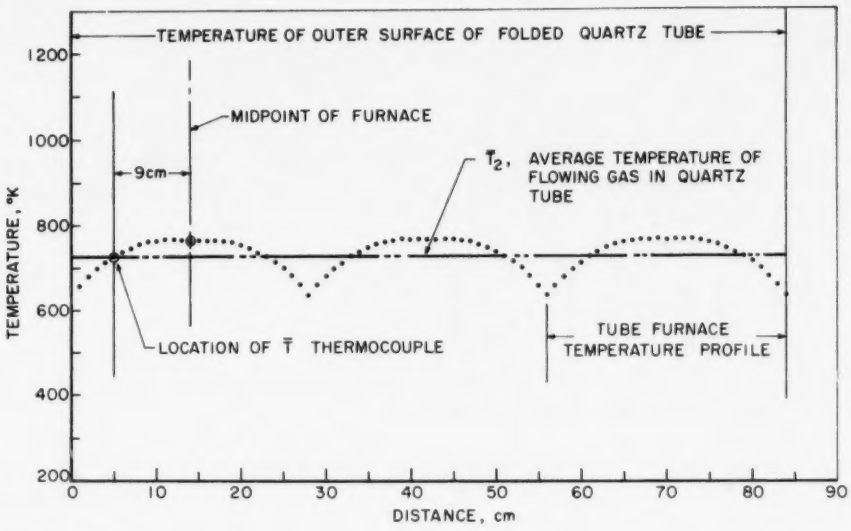



Figure A5. Temperature profile of quartz tube furnace.

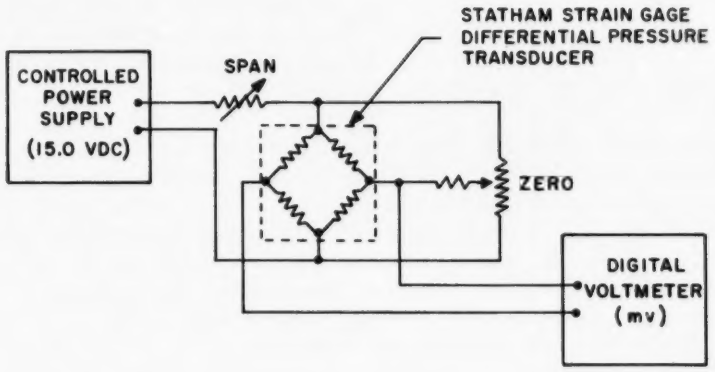



Figure A6. Electrical schematic of pressure transducer.

Once the sample molecules or fragments and products thereof have passed through the high-temperature quartz tube, they are trapped in or on the sorbing medium of the effluent trap. This trap is then removed from the high-temperature apparatus and a quantitative standard is deposited in the trap. The contents are then subjected to a programmed-temperature gas chromatographic analysis using a modified Tracor 550 instrument.

The injector of this gas chromatograph has been modified so that it will accept the Pyrex tube containing the trapping medium and its sorbed sample. Modifications to the chromatograph are such that thermal desorption of the trapping medium can be conducted while it is positioned just upstream of the column packing (see Figure A7). This is accomplished by means of a cartridge heater embedded in an aluminum block which surrounds the inlet region of the glass column. By heating this inlet region to 270°C for 10 minutes, the trapped effluent is completely desorbed. Since this desorption is made with the chromatographic oven at room temperature, the products are swept from the trapping medium and deposited on the inlet portion of the packed column.

After a suitable thermal desorption time (10 minutes), the chromatographic oven is closed and the column temperature is programmed, thereby separating and subsequently detecting the various organic products. With this trapping and thermal desorbing technique, essentially quantitative collection and transfer has been achieved for organic compounds in the molecular weight range of 150 to 550.

With this apparatus, the effect of residence time on high-temperature degradation can be readily determined. Samples can be subjected to successive tests at a constant $\bar{T}_2$ but with different volume flow rates, that is, different residence times. The trapped effluents from these tests can then be analyzed, thus permitting an evaluation of the effect of $\bar{t}_r$ on thermal destruction at a given temperature.

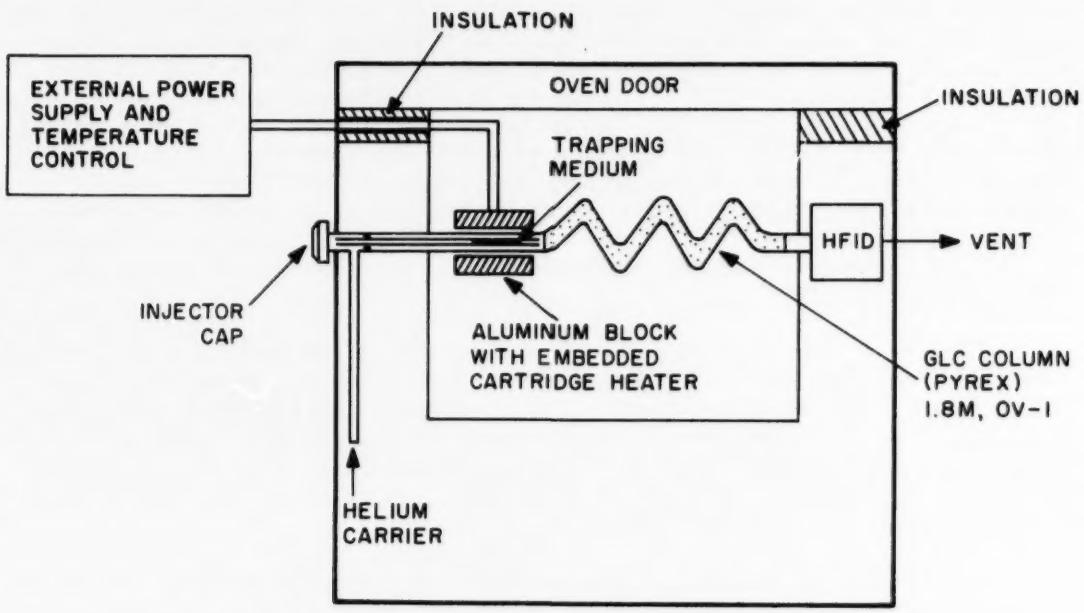



Figure A7. Interior of modified Tracor 550.

## APPENDIX II

## ERROR ANALYSIS OF MEAN RESIDENCE TIME DETERMINATION

Earlier, equation (A.I.6) described the mean residence time of a substance as it passed through a high-temperature quartz tube. This residence time equation,

$$\bar{t}_r = \left(\frac{\pi r^2 L}{F_o}\right)\left(\frac{T_o}{\bar{T}_2}\right)\left(1 + \frac{p_d}{p_o}\right) \quad . \tag{A.II.1}$$

contains many variables, some of which have a pronounced effect on $\bar{t}_r$ and are difficult to measure.

Upon investigation, it is found that fused quartz has a very small coefficient of expansion (approximately $0.59 \times 10^{-6}$). Therefore, for a given tube, the radius r and the length L can be assumed temperature invariant. Thus, the effective volume of a specific quartz tube, i.e.,

$$V_t = \pi r^2 L \quad , \tag{A.II.2}$$

remains essentially constant.

Further, the laboratory temperature $T_o$ and pressure $p_o$ can be easily and accurately measured. However, the outlet ambient flow rate $F_o$, the average oven temperature $\bar{T}_2$, and the system differential pressure $p_d$ require special measurement equipment.

The maximum change in $\bar{t}_r$, which can be attributed to an addition of errors in $F_o$, $\bar{T}_2$, and $p_d$, can be expressed as

$$\Delta\bar{t}_r = \left|\left(\frac{\partial\bar{t}_r}{\partial F_o}\right)\Delta F_o\right| + \left|\left(\frac{\partial\bar{t}_r}{\partial\bar{T}_2}\right)\Delta\bar{T}_2\right| + \left|\left(\frac{\partial\bar{t}_r}{\partial p_d}\right)\Delta p_d\right| \quad . \tag{A.II.3}$$

From equations (A.II.1) and (A.II.2), we find

$$\frac{\partial\bar{t}_r}{\partial F_o} = -\left(\frac{V_t T_o}{F_o^2 \bar{T}_2}\right)\left(1 + \frac{p_d}{p_o}\right) \quad , \tag{A.II.4}$$

$$\frac{\partial \bar{t}_r}{\partial \bar{T}_2} = -\left(\frac{V_t T_o}{F_o}\right)\left(\frac{1}{\bar{T}_2}\right)^2\left(1 + \frac{p_d}{p_o}\right) \quad , \tag{A.II.5}$$

$$\frac{\partial \bar{t}_r}{\partial p_d} = \frac{V_t T_o}{F_o \bar{T}_2 p_o} \quad . \tag{A.II.6}$$

Now the maximum errors typically associated with the selected measurement methods are

$$\Delta F_o = F_o \times 10^{-2} cm^3 sec^{-1}$$

$$\Delta \bar{T}_2 = 5^oK$$

$$\Delta p_d = 5 \times 10^{-3} atm$$

Next, an example case is presented where

$$\bar{t}_r = 1.0 \text{ sec}$$

$$F_o = 1.235 \ cm^3 sec^{-1}$$

$$T_o = 296^oK$$

$$\bar{T}_2 = 873^oK$$

$$p_o = 0.974 \text{ atm}$$

$$p_d = 0.2 \text{ atm}$$

$$V_t = 3.021 \ cm^3$$

By substituting into equation (A.II.3) the data for this case and the typical measurement errors, the worst condition is found to be

$$\Delta \bar{t}_r = \left| \Delta \bar{t}_{r_{(flow)}} \right| + \left| \Delta \bar{t}_{r_{(temperature)}} \right| + \left| \Delta \bar{t}_{r_{(pressure)}} \right|$$

$$\Delta \bar{t}_r = 0.00999 + 0.00575 + 0.00426$$

Thus,

$$\frac{\Delta \bar{t}_r}{\bar{t}_r} = 0.020$$

or, the maximum relative error in $\bar{t}_r$ is 2.0%.

With this instrumentation, the flow measurement possesses about twice the effective error in $\bar{t}_r$ as the temperature or pressure measurement. Also, upon further examination, it is observed that $\Delta\bar{t}_r/\bar{t}_r$ is essentially unaffected by the broad temperature range and the various residence times.

Consequently, this error analysis shows that the individual measurement errors encountered in determining $\bar{t}_r$ are small and in the same domain.

## APPENDIX III

## RESIDENCE TIME VARIATION

The longitudinal dispersion of a gas as it passes through an open cylindrical tube has been thoroughly studied [57,58]. Consequently, in the absence of a retentive or interactive wall surface, the variation in transport of like molecules can be expressed by

$$H \equiv \frac{d(\sigma_x)^2}{dx} = \frac{2D_g}{\bar{v}} + \frac{\bar{v}r^2}{24D_g} \quad , \qquad \text{(A.III.1)}$$

where H is the height equivalent to a theoretical plate (as commonly utilized in chromatography), $\sigma_x$ is the distribution standard deviation in distance units, x is distance, $D_g$ is the intermolecular diffusion coefficient, $\bar{v}$ is the average linear velocity of the gas, and r is the radius of the open cylindrical tube.

From equation (A.III.1) we can write

$$(\sigma_x)^2 = \int_0^{x=L} \left(\frac{2D_g}{\bar{v}}\right) dx + \int_0^{x=L} \left(\frac{\bar{v}r^2}{24D_g}\right) dx \quad , \qquad \text{(A.III.2)}$$

and, at distance x=L

$$(\sigma_x)^2 = \frac{2D_g L}{\bar{v}} + \frac{\bar{v}r^2 L}{24D_g} \quad . \qquad \text{(A.III.3)}$$

Now, for like molecules that are randomly entering and passing through a narrow bore tube, the variation in residence time can be represented by a Gaussian distribution with a time-based independent variable. Thus, it is necessary to convert $\sigma_x$ to a time-based sigma value. This is readily accomplished as

$$(\sigma_x)^2 = (\sigma_t)^2 \, (\bar{v})^2 \quad . \qquad \text{(A.III.4)}$$

Equation (A.III.3) can now be rewritten as

$$(\sigma_t)^2 = \frac{2D_g L}{(\bar{v})^3} + \frac{r^2 L}{24\bar{v}D_g} \qquad \text{(A.III.5)}$$

or

$$\sigma_t = \sqrt{\frac{2D_g L}{(\bar{v})^3} + \frac{r^2 L}{24\bar{v}D_g}} \quad . \qquad \text{(A.III.6)}$$

The intermolecular diffusion coefficient has been equated by Reid and Sherwood [59] as

$$D_g = D_{1,2} = \frac{b}{Pd^2}\left(T^{\frac{3}{2}}\right)\sqrt{\frac{M_1 + M_2}{M_1 M_2}} \quad , \qquad \text{(A.III.7)}$$

where P is pressure, T is temperature, d is distance between the molecular centroids upon impact, $M_1$ and $M_2$ are the respective molecular weights, and b is a constant.

Due to the absence of high-temperature diffusion data for ∿400 MW compounds in air, it was necessary to select a model compound for which $D_g$ data did exist. Calculated $D_g$ data could then be obtained with the use of equation (A.III.7) for a broad range of compounds.

The selected model compound was naphthalene. This substance is low enough in molecular weight that $D_g$ data are available, e.g., $D_g$ for naphthalene in air = 0.0611 $cm^2$ $sec^{-1}$ at 298°K and 1.0 atm [59], and it is a common household pesticide. Also, naphthalene is structurally similar to other fused-ring compounds, e.g., aldrin, carbaryl, dichlone, dieldrin, endrin, and the halowaxes.

Next, from the diffusion expression, i.e., equation (A.III.7), it is observed that

$$\frac{\partial D_g}{\partial T} = \frac{3b}{2Pd^2}\sqrt{\frac{T(M_1 + M_2)}{M_1 M_2}} \quad . \qquad \text{(A.III.8)}$$

Therefore, even with fixed values of P, r, L, and residence time, $\sigma_t$ will continue to vary with temperature and $M_2$ (the molecular weight of the larger component).

To clarify this situation, residence time distribution data, as represented by $\sigma_t$, have been calculated and plotted for the specific case where molecules experience a 1.0 sec residence time while passing through a tube 84 cm in length by 0.8 mm inside diameter with an internal pressure of 1.2 atmospheres. These calculated $\sigma_t$ data which are presented in Figure A8a encompass the temperature range of 298°K to 900°K, and the molecular weight range of 128 (naphthalene) to 546 (Mirex).

Another graph was prepared, again from calculated data, where $\sigma_t$ was plotted versus residence time for naphthalene at 700°K and 1.2 atmospheres. This information is presented in Figure A8b.

From information contained in Figures A8a and A8b, a number of conclusions can be drawn. First, from Figure A8a, it is observed that molecular scatter, or variation in residence time, is small. As an example, it is seen that at 700°K the residence time for 95% of the naphthalene molecules would fall within $1.0 \pm 2\sigma_t$ seconds, that is, between 0.96 and 1.04 seconds. Secondly, it is observed from this same figure that the molecular weight of the vaporized compound has only a small effect on $\sigma_t$. This is evidenced by the narrowness of the molecular weight band. Thirdly, it is observed that molecular scatter is strongly dependent upon temperature. In fact, although the intermolecular diffusion coefficient increases with temperature, the residence time distribution, as represented by $\sigma_t$, decreases with temperature.

Figure A8b shows the variation of $\sigma_t$ with $\bar{t}_r$ for naphthalene. Upon further investigation it is determined that the term $4\sigma_t/\bar{t}_r$ varies only by a factor of two over the residence time range of 0.3 to 2.0 seconds. Thus, the relative change in $\sigma_t$ with $\bar{t}_r$ is tolerable.

Lastly, it is important to note that $\sigma_t$ is strongly dependent upon the tube radius r. It is seen from equation (A.III.6) that as r increases, the residence time distribution broadens. Thus, for a small variation in molecular transport time, a quartz tube with a narrow bore is required.

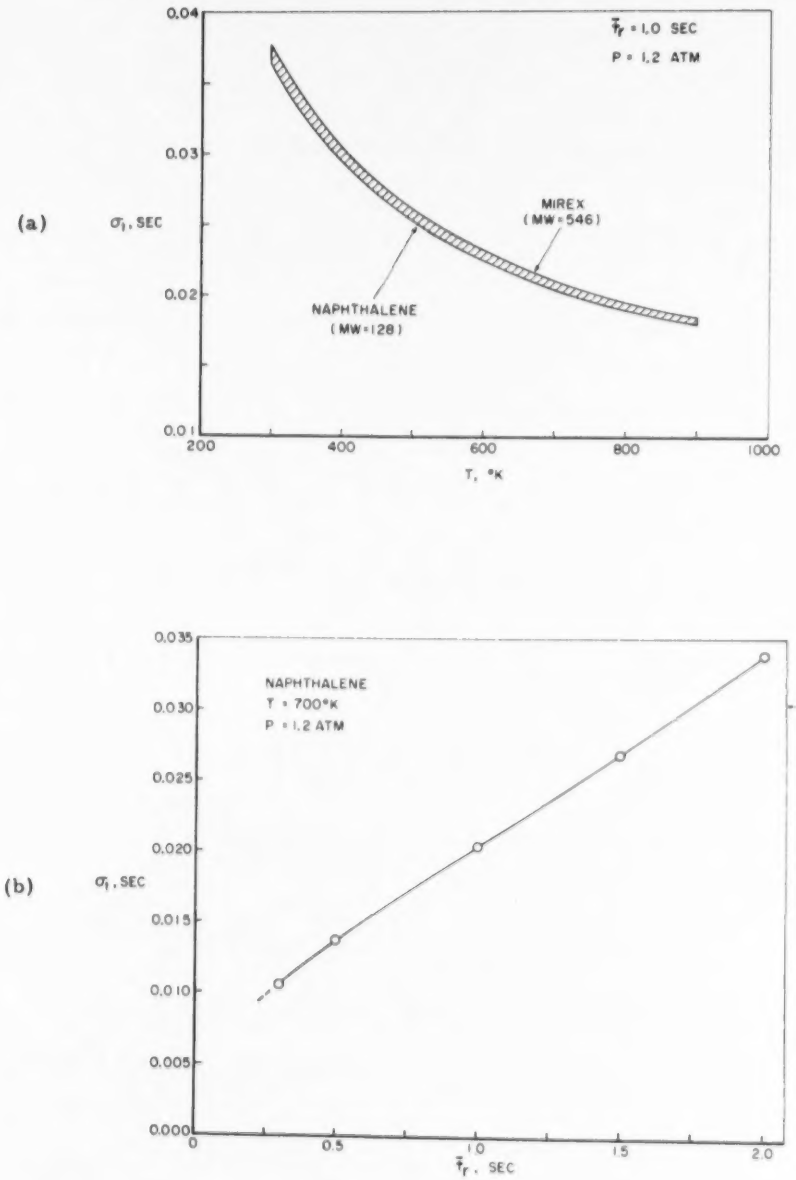



Figure A8. Residence time distribution data.
(a) Effort of temperature and molecular weight
(b) Effect of residence time

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